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THE

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LOSS OF VELOCITY OF CATHODE RAYS IN MATTER

By H. M. Terrill

Abstract

Loss of energy of cathode rays in passing through metallic foils.—Whiddington's apparatus was modified to provide a bundle of homogeneous rays by fitting a Coolidge cathode into a high vacuum tube and exciting it by rectified high tension current of accurately known voltage. After traversing the metal foil, the electron beam is deflected by the magnetic field of a solenoid and is spread into a broad band of which a small section, deflected about 30°, passes through a fixed slit into a Faraday cylinder connected to an electroscope. By varying the solenoid current, energy distribution curves were obtained, and the most probable energy loss for each case was determined from the position of the maximum. Rolled foils of *Ag, Al, Au, Be and Cu* were studied, for 25 to 51 kv, giving rays of 9 to 12.6×10^9 cm/sec. velocity. The results agree with the velocity formula of J. J. Thomson, $v_0^4-v_x^4=ax$, where x is the thickness, and a is a constant which comes out proportional to the density of the metal so that $a/\rho=5.05\times10^{42}$ approximately. In the corresponding voltage formula $V_0^2-V_x^2=bx$, $b/\rho=.40\times10^{12}$.

OBSERVATIONS of the passage of cathode rays through matter were made by Lenard[1] as early as 1894 and some measurements of the loss of velocity were obtained by Leithauser[2] about ten years later, but these results were mainly qualitative. Whiddington[3] measured the velocity loss in thin sheets of gold, copper and aluminum, and his results agreed with the law previously deduced by J. J. Thomson:[4]

$$v_o^4-v_x^4=ax \qquad (1)$$

where v_o is the velocity of the entering electrons, v_x the most probable velocity of the emerging, x the thickness, and a the constant for the metal. In a later article he gives values of the constant a for tin, silver and platinum obtained from absorption measurements. Von Baeyer[5]

[1] Lenard, Ann. der Phys. u. Chem. **52,** 1894.
[2] Leithauser, Ann. der Phys. **15,** 299, 1904.
[3] Whiddington, Proc. Roy. Soc. **86,** 360, 1912; **89,** 559, 1914.
[4] J. J. Thomson, Conduction through Gases, 378.
[5] Von Baeyer, Phys. Zeit. **13,** 485, 1912.

using slow β rays from mesothorium-2 made a large number of measurements for the velocity loss in aluminum by a photographic method. His results agreed approximately with the above law but gave a somewhat higher value of the constant than obtained by Whiddington. The results of Danysz[6] and Rawlinson[7] were obtained by photographic methods with higher speed β rays and seemed to give approximate agreement with a theoretical relation obtained by Bohr[8] which was expressed in terms of the magnetic field required to deflect the rays. Becker[9] has proposed an expression for the value of dv/dx and Lenard[10] has plotted values of this quantity from the collected results of previous papers, without attempting to give an analytical expression for the law followed.

Method

The present method is a modification of Whiddington's. Using a gas filled tube, Whiddington controlled his initial velocity by spreading the rays into a magnetic spectrum which could be passed over the entrance slit. The final velocity was measured by deflecting the rays in a second magnetic field, the deflections being read by permitting these rays to strike a fluorescent screen. In both cases, the velocities had to be determined from the deflections by calculations based on the dimensions of the coils and currents used.

In the present apparatus, the source of electrons is a Coolidge cathode, the initial velocity being controlled by the applied voltage. The final velocity is measured by magnetic deflection, but the velocities are determined from the field currents which have been previously calibrated by observations on the direct beam. In this method, no errors are introduced by non-uniformities of the field. Instead of observing the impact of the deflected beam upon a fluorescent screen, it is received upon a slit, beyond which is a collecting plate connected to a gold leaf electroscope.

Apparatus

The general outline of the tube is shown in Fig. 1. It consists of two bulbs and a long neck, closed at the top with a removable plug, the joint being accurately ground and sealed with stop-cock lubricant. The stem bearing the cathode is attached to the plug. The tube itself

[6] Danysz, Le Radium, Jan. 1912.
[7] Rawlinson, Phil. Mag. **30**, 627, 1915.
[8] Bohr, Phil. Mag. **25**, 10, 1913; **30**, 581, 1915.
[9] Becker, Sitzungber. Heidelb. Akad. **4**, 1917.
[10] Lenard, Quantitatives über Kathodenstrahlen, Heidelberg, 1918.

is mounted in a transite oven with the long neck projecting through the top so that the ground joint may be kept cool during the baking out process by being wrapped with a wet cloth. For evacuation, a mercury condensation pump backed by a Gaede rotary mercury pump and a fore pump was used, the pumps being run continuously while the tube was operating. A slush of carbon dioxide snow in acetone

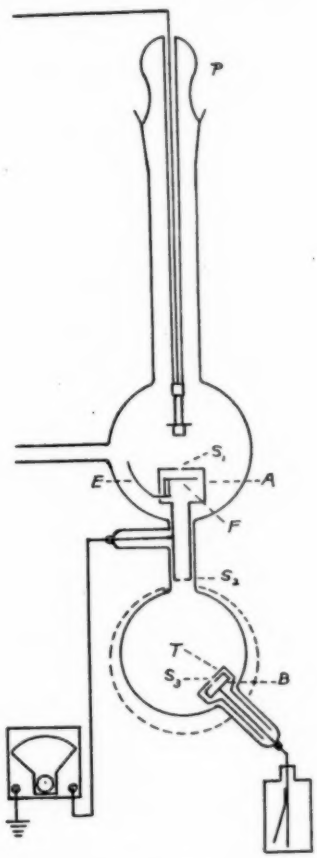

Fig. 1. Diagram of apparatus

was used around the trap to keep out mercury vapor. Before each run it was necessary to bake out at a temperature of about 300°C; then the oven was partially dismantled and the solenoids and electroscope fitted in place.

Referring to Fig. 1, the anode *A* is removable and of such size that it may be inserted and withdrawn through the neck. When in place, electrical connection is secured by its bearing against a small brass

spring projecting from the side tube just below the main bulb. The anode is constructed of brass, faced with copper, and is hollow, providing space for a light metal frame F, carrying the foil. This frame is pivoted, and an attached steel rod E, projecting from the side of the anode may be moved by a magnet outside the tube, so that the foil may be swung clear of the electron stream when desired. The slits S_1 and S_2 are about 9 cm apart; various widths were tried, the best results being obtained with a width of ½ mm.

The lower bulb provides space for spreading the beam into a magnetic spectrum and contains the receiving slit S_3 cut in a grounded metal shield T, inside of which is the collecting box B. The slit is so placed that the electron stream must be deflected about 30° to enter it. In the first tube constructed, the slit was placed so that the beam was bent through 90°, but the wide dispersion so weakened the intensity that readings were very difficult, and better results were found possible by deflecting through a smaller angle. The face of the shield is coated with powdered willemite so that the position of the beam may be roughly located from the fluorescent spot and approximate adjustments of the rheostats made before readings are started. The collecting box is a Faraday cylinder supported on silica insulators and connected directly to a gold leaf electroscope, the connection being made as short as possible in order to keep the capacity small. The image of the gold leaf is projected on a ground glass screen and the time of charging up observed with a stop watch. The grounding key is placed inside the electroscope case. A film of tungsten, evaporated on the walls of the lower bulb, and a platinum wire, sealed just through the surface, provided a ground connection to prevent the walls from becoming charged.

The magnetic field was obtained from two solenoids connected in series and placed outside the lower bulb, the gap between them being about 2 cm. Their cross section is indicated by the dotted circle. Their combined length was 64 cm, and the diameter about 15.5 cm, the winding being composed of four layers of No. 20 enamelled copper wire, 20 turns/cm. The current for these coils, which varied up to about .8 ampere, was supplied by storage cells and was measured by a precision ammeter to about .001 ampere.

The source of high tension current was a transformer supplied by a 500 cycle generator. The current was rectified by kenotrons, and a large glass plate condenser in parallel with the tube maintained the voltage at a constant value. The voltage was measured by an electrostatic repulsion voltmeter, previously calibrated against a 20 megohm metallic resistance, and could be controlled and measured to within

½ per cent. The currents used ranged as a rule from .2 and .5 milliampere, but for certain readings, currents as high as 3 milliamperes were required.

Procedure

To determine the current required to deflect rays of each velocity into the receiving slit, the metal foil was swung clear of the entrance slits, the tube was excited and the direct beam was allowed to pass into the lower bulb, the current in the solenoids being adjusted by rheostats until the beam entered the receiving slit. A reading was made of this current and also of the voltage applied to the tube; and this operation was repeated over the whole range of voltages used, at intervals of about two kilovolts. These readings were plotted and gave a calibration curve. A new curve was constructed for each run in order to prevent error from the solenoids not being returned exactly to their original positions after being removed for baking out the tube.

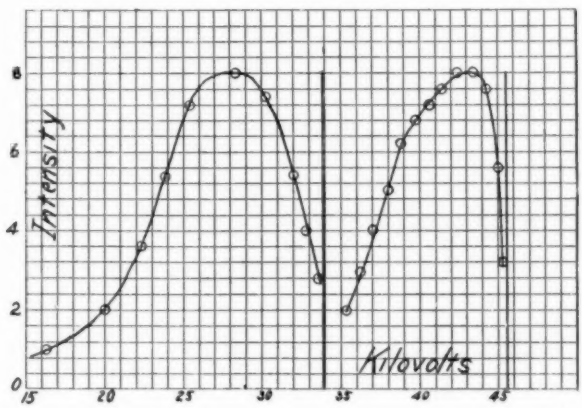

Fig. 2. Velocity distribution curves

The image of the direct beam on the fluorescent surfaces near the slit was narrow and sharp, proving that the condenser capacity was sufficient to smooth out the voltage undulations. Occasionally the sharp image would be accompanied by a fainter diffuse one on the low velocity side. This was presumably due to electrons reflected at nearly grazing incidence from the sides of the slit and was always gotten rid of by adjusting the cathode over the center of the slit.

When the metal foil was swung into place, the sharp image of the direct beam gave place to a diffuse band with a maximum of brightness toward the high velocity end. The distribution of intensities in this band for .00031 cm aluminum and initial voltages of 33.9 and 45.6 kv,

is shown in Fig. 2. These curves were obtained by varying the current in the solenoids by small amounts, thus passing the spectrum across the face of the receiving slit, and reading the rate of charging of the electroscope for each current. As a rule, a distribution curve was not drawn for each applied voltage. The position of the maximum is all that is here required, and this can be located by a very few points.

Velocities were computed from voltages by using the relation $V = 2.830\times10^{-16}v^2\ (1+.83v^2\times10^{-21}+.77v^4\times10^{-42})$, which retains three terms of the series.

Results

Table I gives the results for aluminum of two different thicknesses. Within the limits of experimental error, these quantities satisfy the voltage equation corresponding to Eq. (1)

$$V_0^2 - V_x^2 = bx \qquad (2)$$

and the mean value of b is 1.1×10^{12}. This corresponds to a value of a in Eq. (1) of about 1.4×10^{43}. This value of a is considerably higher than that obtained by Whiddington ($.732\times10^{43}$), and somewhat higher than the value given by Von Baeyer (1.1×10^{43}), but it is in good agreement with the value obtained by Bohr from theoretical considerations. In the first paper, Bohr[8] gives the value for a as 1.9×10^{43}, but in the second paper, he concludes that this value is too large by the factor 1.3, for the range of velocities here considered, and this reduces his value of a to 1.46×10^{43}.

Table I

Aluminum foils

Thickness (cm)	V_0 (kv)	V_0^2 (kv)	V_x	V_x^2	$V_0^2-V_x^2$
.00031	24.6	605	16.9	285	320
(one sheet)	29.8	888	22.6	510	377
	35.6	1267	29.6	876	391
	40.9	1672	36.8	1354	318
	45.8	2097	42.2	1780	317
	51.2	2621	48.1	2313	308
.00062	34.5	1190	22.2	493	697
(two sheets)	42.2	1780	33.5	1122	658
	46.3	2143	38.3	1466	677
	51.0	2601	43.7	1909	692

The only other metals that could be obtained in thin sheets suitable for this work were copper, silver, gold and beryllium. I wish to express my obligations to Dr. C. S. Brainin, of Baker and Co., for aid in securing sheets of these metals suitable for the work. In every case, the sheets were made by rolling, rolled foil being more homogeneous and in other

respects superior to beaten leaf. In the case of gold, the sheets were required to be of such extreme thinness that it was necessary to overlay a sheet of copper foil with gold and roll out the combination, then dissolve the copper in nitric acid.

The thickness was determined in each case by weighing a sheet of known area. Runs were made with pieces cut from different parts of each sheet in order to average out, in the mean results, any possible errors due to variations in thickness.

Table II gives mean values of the readings obtained.

TABLE II

Metal	Thickness (cm)	V_0 (kv)	V_z (kv)
Silver	.00023	41.7	27.1
		46.1	33.2
		49.8	37.1
Gold	.00012	46.1	30.1
		48.0	33.2
Beryllium	.0025	48.0	16.7
		50.5	20.0
Copper	.00024	36.8	23.1
		40.5	27.1
		45.3	33.2
		50.5	40.0

The values of the constants a and b are given in Table III.

TABLE III

Metal	a (10^{43})	b (10^{12})	ρ	b/ρ (10^{12})	σ (10^{22})	b/σ (10^{14})
Beryllium	0.94	0.75	1.9	.39	51	147
Aluminum	1.4	1.1	2.7	.41	78	141
Copper	4.5	3.6	8.9	.40	244	147
Silver	5.3	4.2	10.5	.40	274	153
Gold	11.2	8.9	19.3	.46	464	192

The accuracy of the values found for these constants should be much higher than values previously given, since the position of maximum intensity of the velocity spectrum was obtained by direct measurements; all previous results were obtained by optical methods applied to fluorescent screens and photographic plates. Other favorable features of the present method are the use of a Coolidge cathode, giving a homogeneous beam of cathode rays with constant potential direct current; accurate voltage determinations based on measurements with a metallic high resistance; and the use of rolled foil rather than beaten leaf.

The value of a for gold obtained by Whiddington is 2.54×10^{43}. The ratio of his values for aluminum and gold is approximately the same as the ratio of the present values for aluminum and copper. The constant for gold given by Bohr, corrected in the same manner as that for aluminum, comes out equal to 5.6×10^{43}. It should be remarked that Bohr's values include a factor that must be obtained from experiments with α rays, and the experiments from which this data was obtained are less accurate for gold than for aluminum, as shown by the values of the atomic numbers computed from the same data.[11] The constancy of the values of b/ρ given in the table shows that the value of b is proportional to the density.

A piece of mica used in the apparatus gave approximately the same values of the constant as aluminum. The observations in the case of mica are less trustworthy, since it is difficult to split mica into sheets that are sufficiently thin and at the same time uniform, but as the density of mica is about the same as that of aluminum, the agreement of the constants is additional evidence in favor of the relation $b/\rho=\text{const.}$

It is possible that b depends on the number of electrons per cubic centimeter, which is not exactly proportional to the density. Calling it σ, we have $\sigma=\text{density}\times\text{atomic number/atomic weight}$.

The values of σ for the metals used are given in Table III together with the values of b/σ. The values of b/σ come out approximately constant, but not quite so closely as the values of b/ρ.

Values of the constant b for molybdenum and tungsten are desirable for application in x-ray theory, but these metals cannot be used in the present apparatus as they cannot be obtained in foil of the required thinness. However, assuming $b/\rho=.40\times10^{12}$, we may compute b and obtain the values, molybdenum 3.6×10^{12} and tungsten 7.6×10^{12}.

It is hoped to give some further results in a later paper, particularly in reference to the distribution curves.

In conclusion, I wish to thank Prof. Bergen Davis, who suggested the research, for his kind interest and helpful advice.

PHOENIX PHYSICAL LABORATORIES,
COLUMBIA UNIVERSITY,
February 15, 1923.

[11] Bohr, loc. cit. p. 27.

VARIATION WITH PRESSURE OF THE RESIDUAL IONIZATION OF GASES

By Hal F. Fruth

Abstract

Residual ionization in air, nitrogen, oxygen and CO_2 under high pressures.—The measurements made by K. M. Downey for air using a steel sphere of one foot inside diameter, have been extended to pressures of 75 atmospheres. (1) *Purified gases.* Air and oxygen gave curves for ionization vs. pressure, first slightly concave upwards (1-15 atm.) then concave downwards (15-35 atm.), then concave upwards (35-53 atm.), then horizontal, the values increasing from 8-10 ions/cc/sec. at 1 atm. to 62-68 for 60 atm. For CO_2 the horizontal part was reached at 61 atm., the limiting value being 97 ions/cc/sec. (2) *Gases containing dust and water-vapor* gave similar curves except that the ionization did not reach a limiting value but continued to increase. (3) *Anomalous behavior of nitrogen.* When prepared from air by the liquifaction process, or by absorption of the oxygen by alkaline pyrogallate, nitrogen showed no upper limit with increasing pressure, either alone or when mixed with oxygen, although air showed this limit. Evidently the process of preparation used, either introduced some long period radioactive impurity or gave the nitrogen some peculiarity such as a tendency to ionize spontaneously. (4) *Penetrating radiation* can apparently be responsible for only a small part of this ionization, not more than 1 ion per cc per atm. per min. as otherwise it would not reach a limit and would not depend so much on the purity of the gas.

Introduction

IT IS a well known fact that there is a seemingly spontaneous ionization in gases in closed vessels. It is generally conceded that this ionization is too great to be wholly accounted for by the known radioactive substances in the soil, air and surrounding materials. The surplus ionization is generally termed "residual ionization" and is often attributed to an ionizing source from without the vessel, called the "penetrating radiation." A large number of observers have studied this radiation, especially McLennan,[1] Wigand,[2] Wilson,[3] Gockel,[4] Swann,[5] and Downey.[6] The last named observer made a special study of the residual ionization and its variation with pressure, and obtained a linear relation up to 20, and

[1] McLennan, Phil. Mag. **26,** pp. 740-752, 1913; Phys. Rev. **26,** pp. 526-631, 1908.
[2] Wigand, Phys. Zeit. **18,** pp. 1-6, 1917.
[3] Wilson, Proc. Cam. Phil. Soc., **11,** pp. 32, 1900; **11,** pp. 428-430, 1902.
[4] Gockel, Phys. Zeit. **16,** pp. 345-352, 1915.
[5] Swann, Bull. Nat. Res. Coun., **17,** pp. 65-73, 1922.
[6] Downey, Phys. Rev. **16,** pp. 420-437, 1920; **20,** pp. 186-193, 1922.

a slowly decreasing slope up to 40 atmospheres pressure. In a later work, however, she obtained a saturation value at 46 atmospheres. The object in the present investigation was to carry out some of the above mentioned experiments at higher pressures with greater sensitivity and to study the natural ionization with respect to pressure and other conditions, such as age, dust and moisture, in air and in other gases in order to try to throw light upon the nature of the agency causing this ionization.

Description of Apparatus

The form of the apparatus was suggested by Prof. W. F. G. Swann. The general arrangement is shown in the diagram Fig. 1 and the ionization chamber, one of the cast-steel spheres used by Dr. Downey, was 1 ft in internal diameter and had a capacity of 14.8 liters. The walls were 1 inch thick. The two hemispheres of which it was composed were held together by twenty-four ¾ inch bolts and screws. Red rubber gaskets were used between the hemispheres and great force was applied to the screws until a pressure of 85 atm. could be sustained. A hard rubber ring and cone, coated with resin and bees-wax, and separated by a brass guard ring, were used at the point where the central electrode entered the sphere. The central electrode consisted of an iron rod 10 in. long. Its outer part was connected to the inside of a subsidiary condenser C, the outside of which was fastened to, but insulated from, the steel sphere. This central system was connected to one pair of quadrants of a quadrant electrometer. The sphere and the outside of the condenser C were connected to the opposite ends of a high resistance, immersed in oil, which in turn were connected to a high tension battery of storage cells. A point between the terminals of the high resistance was joined to the electrometer case as were also all shields and guard rings.

This arrangement is adapted to measurements of high accuracy as it readily compensates for any effects due to fluctuations of the battery.[7] The potential of the needle of the quadrant electrometer was kept at 100 volts by a battery of high constancy. The system was kept balanced by moving the point of contact between the terminals of the high resistance and by altering the capacity of the variable condenser C, until a point was reached where $Q=CV=C'V'$, i.e. where voltage times capacity on one side equals voltage times capacity on the other. If this condition holds, the voltage across the high resistance may be thrown off and on without causing a deflection of the needle when the central system is freed from earth. In the present work such refinement

[7] W. F. G. Swann, Phys. Rev. **17**, pp. 240-242, 1921.

was obtained that 1,000 volts could be thrown off and on the resistance without causing a deflection of more than 1 mm of a spot of light reflected from the mirror on the needle, upon a scale 1 meter away. Since a fiber sensitive to 1,000 mm per volt was used, the effect is roughly the same as if the battery were constant to one part in one million.

To facilitate the use of a null method, a potentiometer system D with a voltmeter W was used to keep the deflection at zero while the central system was being charged by the ionization current.

All parts of the system were supported on plugs of sulphur, the material also used to insulate every part of the central system, except as described above. The parts of the insulated system not otherwise shielded were

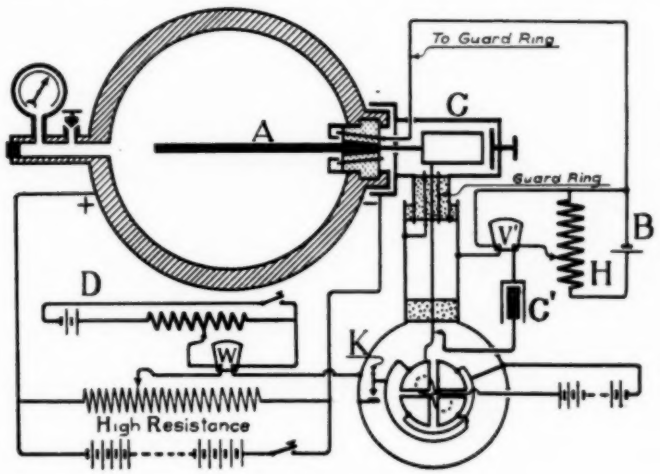

Fig. 1

surrounded by shields connected to the electrometer case. Guard rings were used to protect the central system against any leakage from points of high potential; these were, of course, connected to the electromteter case.

Method and Calculations

If V is the alteration in potential recorded by the voltmeter W during the time t, while the electrometer needle is kept at zero deflection, the rate at which charge leaves the central system is kV/t, where k is a constant, and the rate of production of ions per cc in the vessel is $Q = kV/etv$ where v is the volume of the sphere (14.8 liters), and e the elecronic charge (4.8×10^{-10} e.s.u.).

The constant k was determined by means of the device H (Fig. 1). A known voltage V' was put on the outer member of the condenser C'

whose inner member was joined to the central system. The central system was released from the electrometer case, and the capacity of C' was changed by a known amount ΔC, the resulting deflection being brought back to zero by means of the potentiometer system D. The change of reading R of the voltmeter W was noted and the constant k was obtained from the relation $V'\Delta C = kR$.

In obtaining the relation between $V'\Delta C$ and R as described above, a considerable difference was found according as the plus or the minus terminal of the cell B was connected to the outside of the condenser C'. Experiment showed that this was due to a contact potential between the inner and outer cylinders of the standard condenser C'. This was eliminated by taking the mean reading for V' corresponding to equal positive and negative potential applied to C'.

Voltages necessary for practical saturation. It was necessary to ascertain the minimum voltage required to produce any assigned approximation to saturation. The attempt was made to find a point on the voltage-ionization curve where the voltage might be doubled without increasing the ionization current by more than 3 per cent. Thus with 70 atm. air pressure in the sphere, 200 volts produced 61 ions per cc per sec., whereas 500 volts produced 61.5. The change of ionization during the experiment was often greater than this, nevertheless to insure practical saturation a potential of at least 200 volts above this point was used in all the main readings.

General procedure. Pressure in the sphere was obtained from compression tanks and read from a calibrated Bourdon gauge. With the high tension batteries connected across the terminals of the high resistance, the central system was disconnected from the case. After any slight initial kick had subsided, the electrometer spot was brought to its zero mark by means of the system D, and the reading of W was taken. The spot was then kept at zero for four minutes longer and the change in the reading of W was noted. The rate of production of ions per cc was then calculated as indicated above. In view of the fact that the volume of A was about 200 times that of C no correction was necessary on account of the current resulting from ionization in the latter.

All insulation was carefully tested. No leak was detected for periods of 30 minutes under a wide range of temperature and moisture conditions. All the main readings were taken between 7 p.m. and 2 a.m., the interval giving the smallest range of diurnal variation. In any given set of readings the ionization current for the highest pressure was always measured first; the pressure was then released in steps of 2 to 5 atm.

at a time, and the readings taken for each step. All the readings were taken over periods of 4 minutes. No definite relation could be found between the amount of ionization and the time that had elapsed after the pressure was released and before the 4-minute period was begun. The currents over the four-minute periods were very constant; the various values of Q obtained for successive 4 minute periods never differed from each other by more than 2 per cent. It was found necessary to obtain a new balance of the system after every 5 atm. decrease of pressure, as the dielectric constant of the gas in the sphere and, therefore, the capacity of A varied with pressure.[8] Several calibrations of the

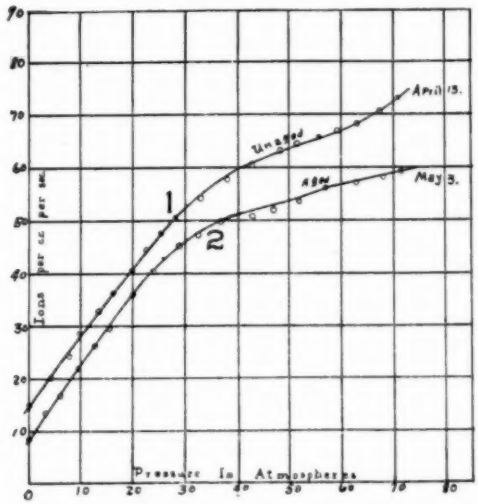

Fig. 2. Results for air, aged and unaged.

system were made using various voltages, and various parts of the condenser C'. A mean value of k was used in all calculations since a value of k obtained when the sphere contained 75 atmospheres of air did not differ appreciably from the mean k.

Results

Unpurified gases. A number of readings on air at one atmosphere were taken and values ranging between 8.15 and 15 pairs of ions per cc per sec. were obtained. Measurements on ordinary air were made over a range of 70 atmospheres. The results are given by curve 1, Fig. 2.

[8] It may be of interest to remark that it is possible to deduce *the relation between dielectric constant and pressure* by observing the change of balance necessary as a result of altering the pressure. The author has measured the dielectric constant of air at various pressures by this method and obtained values agreeing well with those given in Smithsonian Tables.

The air used had been compressed into tanks by the liquid air machine on the previous day and transferred into the sphere three hours before the readings were begun. Curve 2, Fig. 2, obtained 3 weeks later, represents readings on air from the same cylinders. The two curves are parallel up to 27 atm., but the slope of curve 2 at higher pressures is less than that of curve 1. The curves of Fig. 3 give a comparison between the pressure-ionization relations of various gases. All the gases were aged more than 3 weeks to allow most of the radium emanation to decay, but no special effort was made to render them dry and dust free. The slope of the oxygen curve 3 is less than that of air at lower pressures but greater at higher pressures. The nitrogen curve 4 is lower than air and oxygen at 1 atm. but higher and much steeper at higher pressures. The CO_2 curve has a horizontal portion from 61 to 65 atm.

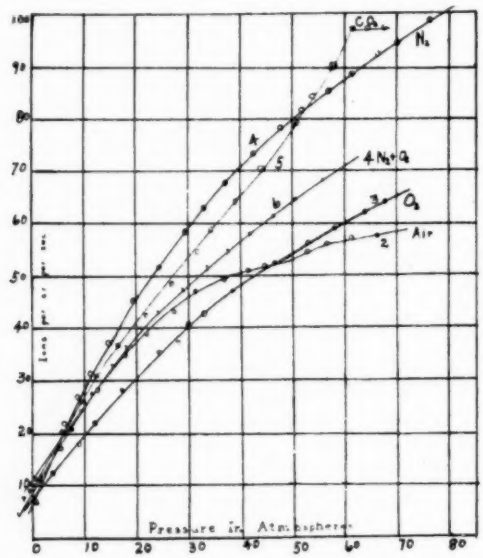

Fig. 3. Results for air, oxygen, nitrogen, CO_2 and $4N_2+O_2$, all at 26°C.

The oxygen curve being lower, and the nitrogen curve being higher than the air curve, one might expect to reproduce the air curve up to 30 atm. by taking readings on a mixture of 4 parts of nitrogen to 1 part of oxygen. A comparison of this artificial air curve 6, with that of ordinary air, curve 2, Fig. 3, shows that the two curves are almost identical up to 27 atmospheres, but the artificial air curve is much steeper at higher pressures. In order to determine whether this deviation of the artificial air curve is due to some radio-active material in the nitrogen, another reading was taken on the same sample of nitrogen 8 days later.

It is known that by far the most important radio-active contamination in a gas is radium emanation, having a half period of 3.8 days. If a gas containing radium emanation is allowed to age, it should show a marked decrease in ionization. A curve obtained from the same sample of gas 8 days later showed no tendency towards a decrease either in initial value or in slope; in fact it was a very close reproduction of curve 4, Fig. 3.

In most curves obtained, it was noticed that, if the curve showed any departure from linearity at pressures below 20 atmospheres and above 1 atmosphere, they would tend to become concave upwards. This tendency was more closely examined, and the results are given in Fig. 4. All curves show a slight tendency towards being concave upwards.

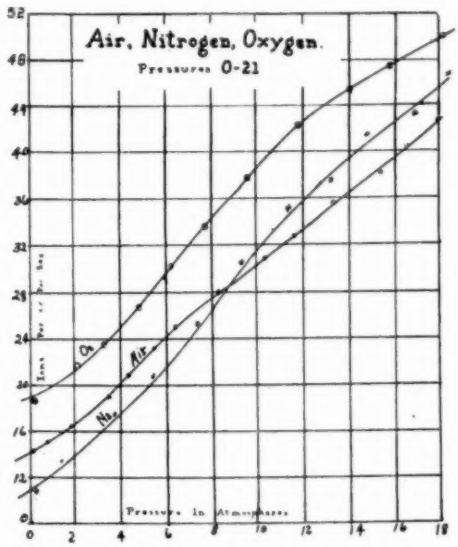

Fig. 4

It might be mentioned at this point that the nitrogen used in this work was purchased from the Cleveland Wire Division of the General Electric Company; it was manufactured by the partial distillation of liquid air, and contained two-thirds of the original amount of argon and all of the neon and helium.

Gases, aged, dried, and dust-free. It was suspected that impurities in gases, especially moisture and dust, would have a large influence upon the pressure-ionization relation. This was definitely investigated by taking readings on gases that had been especially rendered dry and dust-free. The purifying process consisted in passing the gases through

a two inch pipe, 3 feet long, filled with glass wool and cotton to collect the dust, and thence through a similar pipe containing P_2O_5 placed in three trays provided with slanting vanes to cause complete circulation of the gases over this drying agent. The curves obtained from gases thus treated are given in Fig. 5. The oxygen and the two air curves show a decided departure from those of the untreated gases in becoming parallel to the pressure axis at about 53 atmospheres, showing that there

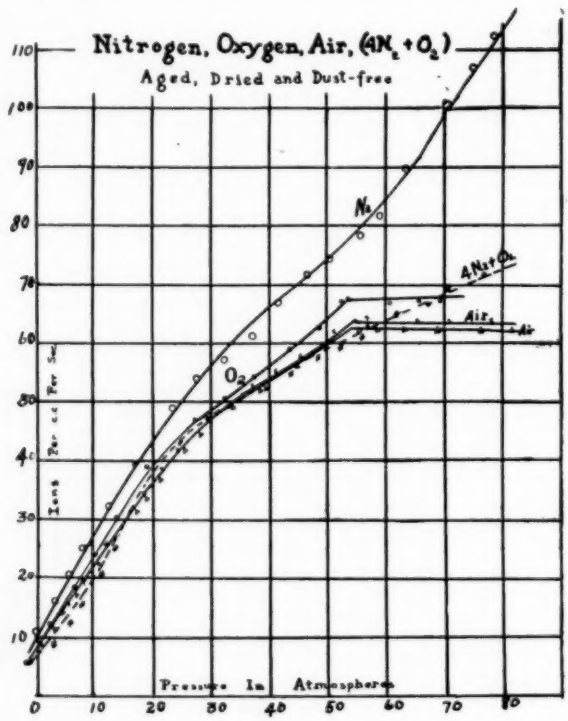

Fig. 5

is no further increase of ionization with pressure. The nitrogen curve is not only much steeper than the others but it also fails to reach a limiting value. The artificial air curve is nearly parallel to the natural air curve up to 52 atmospheres, but it, like the nitrogen curve, does not become horizontal. In order to ascertain whether this exceptional property of the nitrogen curve was due to some peculiar property that this "commercial nitrogen" had acquired during the process of manufacture, the sphere was filled with nitrogen made in the laboratory by absorbing the oxygen from air by means of potassium-pyrogallate. Since the absorption of oxygen had to be carried out at high pressure and on a large scale, a strong iron cylinder of about 7 liters capacity

was nearly filled with potassium pyrogallate, and air was slowly passed through it. Owing to the large amount of heat evolved it was, of course, necessary to cool the cylinder efficiently during the process.

An analysis showed that the nitrogen prepared in the above manner still contained 4 per cent of oxygen. It also contained the original amounts of the inert gases. Readings taken on this gas are shown in Fig. 6. They show the same characteristic features as those obtained from the commercial nitrogen, and fail to show the horizontal portion at the higher pressures. That the existence of this horizontal part in the case of ordinary air is not due, however, to some peculiar property of the oxygen in annihilating the ionization of the nitrogen is borne out by the fact that when nitrogen and oxygen were mixed in the proportions

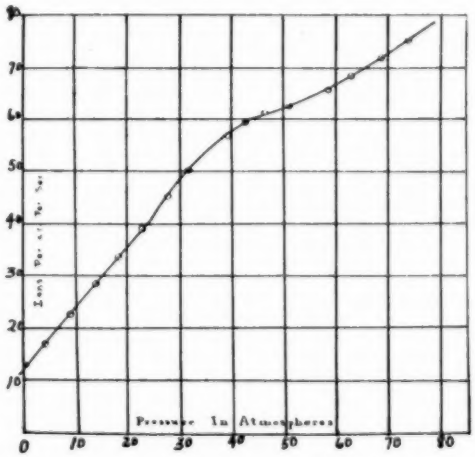

Fig. 6. Results for nitrogen (pyrogallic acid method), aged, dried and dust-free.

to form air, the air so produced was found to give an ionization curve which is approximately the additive resultant of the ionization curves corresponding to the partial pressures of the two constituents out of which it was composed. Fig. 4 shows this clearly in the case of the untreated gases.

It would thus seem that the failure of nitrogen to show the horizontal portion of the curve is due to some peculiarity which it acquires when prepared by either the pyrogallic acid process or by the liquefaction process, and which it retains even when it is again mixed with oxygen. This peculiarity may consist either in the presence of an impurity which is introduced by both methods of preparation, or it may lie in some tendency of the gas to ionize spontaneously for some time after its preparation.

Discussion of Ionization Pressure Relations

Information as to the nature of the agency responsible for the residual ionization should be given by the effects of pressure upon the ionization. If the ionization is caused by the easily absorbable alpha and beta types of radiation from the walls of the vessel it would reach a saturation value at one or two atmospheres pressure in a vessel whose linear dimensions are comparable with the range of alpha and soft beta particles at one atmosphere pressure. An increase of pressure would merely shorten the paths of the radiation, already within the vessel, but it would not increase the number of molecules affected by it, hence the ionization would remain constant. This would be the case if the ionization in these experiments were due to the impurities in the walls of the vessel, for the steel would very probably partake of the ionization character of the soil which, according to Eve[9] is mostly of the alpha type.

If one admits the existence of a radiation which is so penetrating that it is not appreciably absorbed in passing through the air in the vessel even at the higher pressures, its ionization in the vessel may be classified under the following heads:

1) Direct ionization of the gas by the primary penetrating radiation.

2) Secondary ionization by the slowly moving electrons emitted from the gas by the primary radiation.

3) Secondary ionization by the rapidly moving electrons which are emitted from the gas, and whose penetration at atmospheric pressure is greater than the linear dimensions of the vessel.

4) Ionization due to emission of electrons from the walls of the vessel by the action of the primary radiation. This case is indistinguishable from that of ionization by electrons emitted from the walls as a result of radioactive impurities.

Ionization under (1) and (2) should vary linearly with pressure until the pressure becomes so high that the primary radiation itself is absorbed in passing through the vessel. Effects resulting from (3) should vary approximately as the square of the pressure if we assume that the ionization along the path of the electrons is uniform and that these paths are not completed within the vessel, for they would vary with the number of molecules per cc and with the number of ions produced by each electron that is shot out by these molecules when affected by the penetrating radiation. This would cause the curve to become concave upwards. The ionization under (4) should obey a linear law until the pressure becomes so high that all the electrons would complete their

[9] A. S. Eve, Phil. Mag. **21**, pp. 26-40, 1911.

paths within the vessel. At such pressure there would be no further increase of ionization with pressure. But since the ionizing power of the electron is greatest towards the end of its path, the pressure-ionization curve would become steeper shortly before it would become parallel to the pressure axis. If, therefore, complete parallelism should be reached one would be forced to attribute the ionization mainly to (4) i.e., to the emissions of electrons from the walls of the vessel either directly by radioactive contamination in the materials of the walls or by the primary penetrating radiation, and (2) and (3), i.e., the ionization by the direct and indirect action of the radiation *on* the gas, would have to be ruled out as immeasurably small. From a detailed consideration of these factors, Swann[10] has given reasons for believing that in so far as ionization is due to a radiation of a penetrating type, or to secondary rays emitted by such radiation, the rate of production of ions per cc in the open air at one atmosphere is less than, or at most equal to, the rate of production of ions per cc per atmosphere increase of pressure for that portion of the ionization pressure curve where the slope is least, that is about 1 ion per cc per minute.

Discussion of Experimental Results

From a survey of the pressure ionization curves obtained, one can form the following generalizations:

1) In so far as the curves depart at all from linearity at low pressures they show a tendency toward being concave upwards from 1 up to about 15 atm.[11]

2) From 15 to 27 atm. the variation of the natural ionization with pressure obeys a linear law.

3) From 27 atm. upwards there is a large decrease in slope, in most cases, up to about 35 atm. and then another increase.

4) In the cases of the purified gases examined, with the exception of nitrogen, a saturation value is reached at about 52 atm. Shortly before this point there is a rather rapid increase in ionization with pressure.

The results for air are in very good agreement with those of Dr. Downey.[12] Thus, Dr. Downey finds for the range from one atmosphere

[10] W. F. G. Swann, Bull. Nat. Res. Coun., **17**, pp. 65-73, 1922.

[11] This remark does not apply to the region between zero pressure and one atmosphere, for the very considerable magnitude of the ionization at the latter pressure shows that over this range the curve must show a strong concavity downwards. The concavity is very easlly accounted for by α particles which are shot out from the walls of the vessel, and which for the most part complete their range within the vessel before the pressure of one atmosphere is attained.

[12] Downey, Phys. Rev., **20**, pp. 186-193, 1922.

pressure to 27 atm. an increase of 1.23 ion and for the range from 27 atm. to about 45 atms an increase of 0.58 ion per cc per second per atmosphere, while the corresponding results obtained by the writer are 1.23 and 0.60. Also Dr. Downey's curve attained a sharp parallelism with the pressure axis at 46 atm. while the writer's curve attains parallelism at 52 atm.

The upward concavity of the curves in the regions of low pressure as exemplified more in detail in Fig. 4 presents interesting fields for speculation. It could be accounted for by the emission of long range electrons by an external gamma radiation, but if such were its origin we might expect the upward concavity to persist to higher pressures, since the air would not even at the highest pressures, cause an appreciable absorption of the gamma rays. A view which has some advantages is the following. Suppose that as a result of radioactive impurity, or through the medium of an external radiation, electrons are emitted from the walls of the vessel with sufficient range to pass across the vessel. As the pressure is raised each of these electrons will complete more and more of its range within the vessel. The portions of the electronic path near the end of the range are however more active than those near the beginning, so that as the ends of the paths become drawn within the vessel the ionization will increase at an increasing rate with the pressure instead of linearly as it would do if the ionization were constant along the path of the electron. The pressure ionization curve will thus show an upward concavity which will persist until the effect of increased ionizing activity near the end of the path of the electron is counterbalanced by the loss of further increase with pressure on the part of those electrons whose range has been completed within the vessel. When this condition is reached the curve will straighten out and will tend to bend over towards the pressure axis.

While it is possible to account along the above lines for some of the properties of the curves for purified gases, the most striking feature of the curves for purified gases, the suddenness of the attainment of parallelism with the pressure axis, is difficult to reconcile with ionization by any external agency.[13] The sharp breaks resemble those in vapor pressure curves and suggest that the effect may be associated with a gas which begins to condense out at a critical pressure. Then there is the marked change in the characteristics of the curves as a result of the presence of moisture or dust, changes which seem inconsistent with the

[13] An interesting feature is presented by the fact that the maximum ionization in CO_2 is about 1.4 times that in oxygen. If the ionization were produced by the complete absorption of a radiation from the walls of the vessel, we might expect the ionization of different gases to be inversely proportional to the energies necessary to produce an ion. It may be of significance to note that the ionizations *per unit volume* produced by β or γ rays in CO_2 and oxygen are in the ratio 1.4 to unity.

additive nature of the ionization by external agency. Finally there is the anomalous behaviour of nitrogen which has been extracted from the air, as compared with that of the nitrogen in the air. Many of these features receive a more ready explanation on the assumption of a spontaneous ionization in the gas. However, until further data under varied conditions are available, it is hardly worth while elaborating upon this question.

In conclusion the writer acknowledges with pleasure his gratitude to Professor W. F. G. Swann at whose suggestion and under whose guidance the investigation was made, at the University of Minnesota. Thanks are also due to Professor H. A. Erikson for his interest in the work and to Mr. C. H. Dane for help in the mechanical difficulties of the problem.

PHYSICAL LABORATORY,
UNIVERSITY OF MICHIGAN,
March 12, 1923.[14]

[14] The experimental work was completed at the University of Minnesota before June 1922.

THE CONTACT ELECTRICITY OF SOLID DIELECTRICS

By Harold F. Richards

Abstract

The electric charges produced by wringing optically flat surfaces together were measured in order to determine whether or not there is a possibility of formulating a single contact theory which will include both the metals and the dielectrics. Experiments with flint glass and steel proved that the frictional charge is independent of the amount of friction, provided only that intimate contact be established, and is proportional to the area of contact. *The voltaic nature of the frictional charge.* The charge was in no wise affected by the ionization of the residual air molecules between the surfaces by means of an intense beam of x-rays, and was also found to be independent of the duration of contact for periods varying up to 17 hours. The failure of the double-layer to recombine under these conditions proves that it was sustained by a voltaic field. *The dependence of the effect on the dielectric constant.* The charge per cm² Q_{12} of material 1 in contact with material 2, was found for 8 different pairs of the materials, *quartz, fluorite, crown glass, flint glass and steel*, to satisfy, within 14 per cent, the equation $Q_{12}=C(K_1-K_2)$, where K_1 and K_2 are the dielectric constants and C is a positive constant, whose mean value is 4.43 e.s.u., provided the value $K=3.1$ be assigned to steel. This equation is consistent with the results of Coehn's measurements of electric osmosis.

The electric effect of compressing amorphous dielectrics was determined by pressing two kinds of sheet rubber, of dielectric constants 2.94 and 3.96, against seven hard materials, whose dielectric constants ranged from 2.8 to 7.8. The charge on the compressible dielectric was found to be independent of the nature of the material against which it was pressed, proving that this is not a voltaic effect and that amorphous as well as crystalline substances can be electrified by pressure.

The electric effect of collision of a solid insulator and a metal was found, with four pairs of materials, to be consistently opposite in sign to the frictional effect. This result shows that collision must be considered to produce two different effects, one of which is the voltaic charge, while the other is a transfer of electrons from the metal to the dielectric, due in all probability to the inertia of the mobile electrons.

Dielectric constant of steel, as suggested by these results, is not infinity but 3.1.

THE literature of tribo-electricity consists largely of lists in which the various solids are so arranged that any one of them becomes positively electrified when rubbed with a material appearing lower than itself. The singular and disappointing characteristic of these lists is that no two of them are alike.[1] If electrification by friction were

[1] Compare, for example, Shaw, Roy. Soc. Proc. **94**, p. 16, 1917, and Sanford, Phys. Rev. **12**, p. 130, 1918.

an exceedingly small and fugitive effect, the lack of agreement among the data obtained by different experimenters might reasonably be attributed to undetermined contaminations of the surfaces of contact; but the tribo-electric charges are, on the contrary, so large and easily measurable that the inability of one observer to reproduce the results of another, or, indeed, his own, must clearly be referred to other causes. Of the alternative explanations which may be suggested, the most probable and, if found true, the most important, is that the frictional charge results from the superposition, in proportions varying with the manner in which contact is made, of two or more different effects. One of these effects may be expected, if Helmholtz' hypothesis[2] is true, to be exactly similar in nature to the voltaic electrification of two dissimilar metals. Accepting this hypothesis for the moment, and taking account of the fact that the metals are distributed among the dielectrics in most of the available frictional series, we may conclude that a single contact theory can be formulated which will embrace all substances, whether they be good conductors or poor. A unification of theory of such a character is especially desirable because of the fundamental importance of the Volta effect, and the experiments to be described have accordingly been performed with this end in view. The results show that previous discrepancies may be ascribed partly to the impossibility of defining the area over which contact actually occurs in the usual experiment of rubbing a hard solid with a soft buffer;[3] partly to an electric effect of compressing an amorphous material; and partly to the fact that in certain cases the relative velocity of two bodies at the moment of contact determines whether or not an effect due to the inertia of the mobile electrons will be sufficiently large to mask the voltaic electrification. Evidence has been obtained which enables us to speak definitely of the true contact effect of solid insulators; the coefficients of the effect have been measured for several pairs of substances; and these coefficients have been found to depend on the dielectric constants of the materials which are placed in contact.

It seemed perfectly evident from the first that consistent results could be obtained only by carefully defining the area of actual contact. For this reason the first experiments consisted simply in wringing two optically flat disks together, removing one of them, and measuring the electric charge retained by the other. The metal disks were surfaced for this work by the Pratt and Whitney Company, and the dielectric specimens were obtained from various sources. Tests made by the

[2] Helmholtz, Wissenschaftliche Abhandlungen, Erster Band, p. 860.
[3] Cardani, N. Cimento **23**, p. 199, 1922.

method of interference showed that the surfaces were flat to within half a wave-length of sodium light. The apparatus was so arranged that after one of the disks had been removed, the other remained firmly mounted on a brass plate which formed the bottom of a closed, cylindrical brass vessel. When a metal was used as the fixed disk, its charge was shared directly by conduction with the measuring system; and the charge of an insulator could readily be determined by measuring the potential which it induced on the metal vessel surrounding it. This vessel was supported by an ebonite pedestal, and during a measurement was entirely enclosed by an earthed metal shield. Both disks were discharged before they were wrung together, metals by earthing, and insulators by x-raying in air; and the movable specimen was held in a metal socket which remained earthed throughout the experiment. Capacities were determined by comparison with condensers which had recently been calibrated in the Bureau of Standards, and the potentials produced by the frictional charges were measured with a Dolezalek electrometer. There was no trouble on the score of sensitivity, for the charges were so great that capacities as large as 8000 centimeters were required to reduce the potentials to values within the range of an ordinary electrometer having a phosphor-bronze suspension. This instrument was calibrated with a potentiometer and a Weston standard cell.

The Characteristic Coefficient

The dependence of the frictional charge on the area of contact was determined by using, with the same specimen of steel, three glass disks of different sizes, which had all been cut from the same block of flint glass. Typical values of the charge are given in Table I. In the course

Table I

Flint Glass on Steel

Area of contact (cm^2)	Total charge (extremes) (e. s. u.)	Max. variation from mean (percent)	Charge per unit area (mean of 10 tests) (e. s. u./cm^2)
4.99	93–109	9	20.0
3.53	69–80	7	21.1
2.22	46–51	6	21.7

of many experiments it has been found that these results can be duplicated, within the limits of variation shown in the table, at any time; all that is necessary is to clean the flat surfaces with ethyl alcohol and cotton and then allow them to dry completely before a test is made. The usual method of producing intimate contact was to slide the glass

disk across the steel surface and then twist it through a quarter-turn under the pressure of the hand. No effort was made to wring the surfaces together with the same amount of friction at every trial, for many tests showed that after contact had once been established the charge remained independent of the amount of friction. The steel was consistently negative with respect to the glass. So far as the magnitude of the charge is concerned, the figures in the third and fourth columns show that the consistency was not as good with the larger disks as with the smallest one, and the average charge less. The discrepancies are slight, however, and may be referred to the fact that the difficulty of establishing intimate contact over the entire surface increases with the size of the disk. The results show clearly that the charge per unit area is the characteristic coefficient of the tribo-electric effect.

Nature of the Effect

Additional experiments were performed with the flint glass and steel in order to determine whether this effect depends primarily on friction, or on contact. The smallest of the glass disks which had been used in the preceding experiments was wrung upon a flat steel disk, and then the contact interface was irradiated with an intense beam of x-rays. Certainly a good many molecules remain imprisoned between the two surfaces, even when these are optically plane; and it seems evident that the double-layer of electricity could not withstand the discharging effect of the x-rays unless it were maintained by an intrinsic difference of potential arising from the dissimilar natures of the two materials. A Coolidge tube of medium focus was used, mounted at a distance of 33 cm from the contact interface and carrying a current of 30 m-amp at 80 kv; and the long runs were made without melting the target, by operating the tube intermittently. The electrostatic shields surrounding the apparatus were provided with windows of metal gauze to give the x-rays free passage to the specimens, and the beam was so directed as to strike the interface at a small angle after passing through the glass disk. Tests with a fluoroscope showed that the beam was properly directed and amply penetrating. Examples of the results are given in Table II, together with measurements which were made after contacts of long durations. The tests under varying conditions were alternated with others in which the charge was measured after the usual contact of 40 sec., and the results are recorded for comparison. No significance is to be assigned to the particular interval of 40 sec.; this was merely the time ordinarily required to wring the specimens together, close the apparatus, and insulate the measuring system.

In several of the earlier experimens with x-rays, consecutive observations were more consistent than those which had been obtained without irradiating the interface, and so for a time it was thought that the x-rays helped to establish the contact charge. An extended series of observations failed to confirm this conclusion, however, and proved that neither the magnitude of the charge nor the consistency of repeated observations was appreciably affected by the ionizing action of the x-rays. If we assume that a single layer of air molecules remained between the flat surfaces after they had been wrung together, a simple calculation shows that in the absence of a sustaining field the expulsion of one electron from every fifteenth molecule would have reduced the electrification to zero. Since the charge was in no wise diminished we must conclude that the sustaining field was supplied by the steel and the glass. This con-

TABLE II

Flint Glass on Steel
Area of contact interface = 2.22 cm²

Time of x-raying (min.):	1	2	3	8	0	0	
Time of contact (min.):	2	4	8	40	720	1020	
Charge (e. s. u.):	49	51	46	42	40	47	Mean = 45.8
Charge (40 sec. contact without x-rays):	48	50	46	47	48	50	Mean = 48.2

clusion is confirmed by the results of contact of long duration; although after the surfaces had remained in contact for many hours the results were not as consistent as those obtained after shorter intervals, and the average charge was 10 per cent less than the maximum. This discrepancy, however, was easily proved to be entirely too small to account for the recombination which would occur if there were no intrinsic difference of potential. Two disks of the same kind of glass were selected, each having an optically flat surface; and the two surfaces were then electrified with charges of opposite sign but approximately the same magnitude. With fur and silk as buffers the desired electrification could usually be obtained after several trials. The two electrified disks were then pressed into contact, without friction; and measurements made after different periods of contact showed that from 90 to 95 per cent of the charge disappeared during the first five minutes.

Thus the charge is independent of the duration of contact; it is not diminished when the residual air between the surfaces is ionized; and within wide limits it has been found to be independent of the amount of friction. These results show the fallacy of the view[4] that electrification

[4] Jones, Phil. Mag. **29**, p. 272, 1915.

by friction depends primarily on the work done, and we may conclude on this evidence that the only fundamental difference between tribo-electricity and the Volta effect lies in the greater number of points at which contact must take place to produce the characteristic electrification of an insulator. In a recent paper[5] the same conclusion was reached after experiments had shown that the collision of a solid dielectric and a metal produces a quantity of electric energy which does not depend in any direct way on the mechanical energy lost during the impact. It is now known, however, that the conclusion was not valid on that ground; and later on in this article evidence will be given to show that an intrinsic difference of potential is only one of two factors in producing electrification by collision. Other writers have concluded that tribo-electricity is essentially voltaic, because one substance remains positive with respect to another in the frictional series; and Owen, working with surfaces which were not optically flat, furnished additional ground for this view by proving that the work required to produce the maximum frictional charge may be reduced by increasing the pressure of the rubbing surfaces.[6] Recently, important evidence[7] of a different nature has been obtained. Two disks, one of brass and one of glass, were placed in contact with the same surface of mercury, and simultaneous measurements were made of the brass-mercury difference of potential and the glass-mercury contact charge. As the surface of the mercury changed under the influence of the atmosphere, the two effects varied; and when successive measurements of the Volta effect were plotted against the corresponding values of the tribo-electric excitability, the curve was found to be approximately a straight line. This result is entirely consistent with the evidence of the present experiments.

Dependence on the Dielectric Constant

In spite of the essential similarity of the two effects, however, there is good reason for believing that the contact electricity of dielectrics cannot be explained by the accepted theory of the Volta effect. Richardson has pointed out[8] that since at the same temperature two metals emit electrons at different rates, useful work could be gained in violation of the second law of thermodynamics if the metals should come to the same potential when placed in contact; and it is found that if the Peltier heat be neglected, the contact effect of two metals is equal to the differ-

[5] H. F. Richards, Phys. Rev. **16**, p. 290, 1920.
[6] Owen, Phil. Mag. **17**, p. 457, 1909.
[7] E. Perucca, N. Cimento **22**, p. 56, 1921.
[8] Richardson, Electron Theory, p. 455; Nature **108**, p. 374, 1921.

ence of their thermionic work functions. Millikan has recently expressed essentially the same law in terms of Planck's constant and the threshold frequency of the photoelectric emission.[9] Clearly this law cannot be considered adequate to account for the large contact effects of dielectrics, unless the latter can be shown to possess characteristic constants which are analogous to the thermionic work functions of the metals. The dielectric constant suggests itself as the coefficient which is most similar to the thermionic work function, since it is proportional to the ease with which an electron can be displaced within an insulator, whereas the thermionic work function is inversely proportional to the facility with which an electron escapes from the surface of a metal. No experiments of rubbing two solid insulators together have hitherto yielded consistent results which might furnish a test of the similarity of these two constants; but Coehn has succeeded in an admirable series of researches[10] in proving that when a poorly conducting liquid is placed in contact with a solid insulator, the material of greater dielectric constant becomes positive with respect to the other, the difference of potential being proportional to the difference of the two dielectric constants. Coehn established this law by measuring the vertical displacement of current-carrying liquids and combining the results with a relation[11] which Helmholtz had deduced from the theory of the double-layer. The law was verified for twenty poorly conducting liquids in contact with glass, quartz, paraffin, and diamond, and was also found to give the sign of the charge which a gas acquires when it is bubbled through a liquid. Additional confirmation of the law has been furnished by Ulrey's measurements[12] of the metal-liquid contact effect. Nernst's theory of this effect has been attacked by several writers because of the enormous solution-pressures which it assigns to certain of the metals, the pressure of magnesium being so great that it need act through a molecular distance, only, in order to project a magnesium ion into water with a velocity much greater than that of light; and Ulrey has shown that when two similar metals are immersed in different poorly conducting liquids, their difference of potential is proportional to the difference of the dielectric constants of the liquids. Thus there is ample evidence to show that Coehn's law applies not only to the contact of a solid dielectric and a liquid, but to the contact of two liquids as well; and whether or not it describes

[9] Millikan, Phys. Rev. **18,** p. 236, 1921.

[10] Coehn, Wied. Ann. **64,** p. 217, 1898; Ann. der Phys. **30,** p. 777, 1909; **43,** p. 1048, 1914.

[11] Winkelmann's Handb. **3,** p. 499.

[12] Ulrey, Phys. Rev. **12,** p. 47, 1918.

the contact effect of two solids has been tested by measuring the characteristic coefficient of the effect for several pairs of materials.

The results of these measurements are given in Table III. Each value of Q_{12}, the charge per unit area of specimen No. 1 in contact with specimen No. 2, is the mean result of a series of ten or more tests, which were made in the manner previously described. Wringing was used regularly as the method of producing contact; for it was found by

TABLE III

Specimen No. 1	Specimen No. 2	K_1	K_2	Q_{12} (e. s. u./cm.^{2})	C
crown	steel	6.7	3.1	+15.8	4.39
flint	steel	7.8	3.1	+20.9	4.45
quartz	steel	4.6	3.1	+ 7.1	4.73
fluorite	steel	6.9	3.1	+16.0	4.21
fluorite	quartz	6.9	4.6	+ 9.3	4.04
crown	flint	6.7	7.8	− 5.1	4.64
crown	quartz	6.7	4.6	+ 8.2	3.90
quartz	flint	4.6	7.8	−16.2	5.06
flint	flint	7.8	7.8	± 1.5	—
ebonite	steel	2.8	3.1	−18.6	(62.0)

experiment that although easily measurable charges of the usual sign could be obtained by pressing the two surfaces together, without sliding friction, the amount of the electrification produced in this manner, with pressures estimated at 75 kg per cm^2, was only 15 per cent of the maximum. With the exception of ebonite, all the specimens were provided with optically flat surfaces. The ebonite disks, however, became polished when wrung upon a flat surface of steel, so that after an experiment it was easy to estimate the area of actual contact by observing the reflection of light from the surface. The results of several experiments with ebonite disks of different sizes were consistent in such a degree that the value of the ebonite-steel coefficient may be considered quite as reliable as any of the other results. The dielectric constants of fluorite[13] and quartz[14] were taken from published tables, values corresponding to a field in the direction of the optic axis being selected because the flat face of each disk was perpendicular to the axis; and the dielectric constants of flint glass, crown glass, and ebonite were determined directly by measuring larger blocks from which the disks were cut. The constant C is given by the equation

$$Q_{12} = C(K_1 - K_2),$$

where K_1 and K_2 are the dielectric constants of specimens No. 1 and No. 2, respectively. This equation is an expression of Coehn's law, and

[13] Curtis, Phys. Rev. **34**, p. 155, 1912.

[14] Constantes Physiques, Soc. Franc. de Phys., p. 561, 1913.

the agreement among the different values of C is a measure of the extent to which the law has been verified for the materials examined. The dielectric constant 3.1 is assigned to steel as the value giving the most concordant results for C.

The direction of the effect is seen to be consistent with the view that the larger values of K are associated with substances in which the electrons can the more readily be displaced, for C was positive in every case; and the numerical agreement among the different values of C, while not excellent, is sufficiently good to show that the dielectric constant is the important factor in determining the contact effect. Ebonite is an exception, showing no agreement with Coehn's law except so far as the sign is concerned. In all probability the effect depends on $K-1$ rather than K, since $K-1$ measures the difference which may in general be produced by substituting a dielectric medium for free space, and this quantity, of course, satisfies the equation equally as well as K. For the present no attempt is made to interpret the significance of the fact that steel enters the contact series exactly as if it were an insulator having a dielectric constant of 3.1; for an interpretation of this phenomenon should be based upon concordant results for a series of metals, whereas the present type of experiment did not yield sufficiently consistent results to show a definite difference when a nickel disk was substituted for steel. There are other grounds, however, for believing that the dielectric constants of the metals are not infinite, notably the fact[15] that induction takes place freely through very thin metallic films; and Sanford has found,[16] furthermore, that the tribo-electric series contains the insulators in the order of their dielectric constants, the metals being distributed among them in places for which the dielectric constants should be of the order of 4. It is well known that the dielectric constants of many inferior conductors can be measured with rapidly alternating fields, although the conductivity may be so great that static or low-frequency methods are of no avail; and the most recent determination[17] of the dielectric constant of mercury vapor shows that a uniform distribution of fine metallic particles does not greatly increase the dielectric constant of a non-conducting medium. Indeed, the fact that a metallic shield of sufficient thickness furnishes electrostatic protection need not be interpreted to mean that the metal suffers a complete polarization in the Maxwellian sense; for we may consider that the motion of the free electrons masks whatever displacement of

[15] Miss Hyatt, Phys. Rev. **35**, p. 337, 1912.
[16] Sanford, Phys. Rev. **12**, p. 130, 1918.
[17] Bedeau, Comptes Rendus, **175**, p. 147, 1922.

the bound electrons there may be. The results of the present experiments furnish ample ground for the belief that determinations of the characteristic coefficients of a greater variety of materials than those here studied, including substances which are incapable of retaining optically plane surfaces, may be expected to bear significantly on the magnitude of the dielectric constants of the metals.

Effect of Compressing Amorphous Dielectrics

It is well known that compressible dielectrics can be strongly electrified by pressing them against hard substances. This effect, in common with others which have been classified as tribo-electric, has quite generally been regarded as one of the voltaic phenomena. The results which have already been described in this paper, while in no wise proving the truth of this assumption, suggest at once the importance of putting it to the test of experiment. This has been done; and the coefficients of the effect, for a variety of different materials, are recorded in Table IV. The two compressible materials, para rubber and a rubber compound known commercially as pure sheet, were selected because of the large difference of their dielectric constants. These were found to be 2.94 and 3.96, in the order named. Circular sheets of the rubber, 1.6 mm thick, were mounted on flat steel disks, thoroughly cleaned with sandpaper and alcohol, and then placed in contact with various surfaces under pressures ranging from 0.5 to 5 kg per cm². As the pressure was

Table IV

Charge on rubber in contact with	Charge (e. s. u./cm.²) On pure sheet	On para
steel	−21.7	−17.2
shellac	−21.1	−15.5
flint glass	−19.4	−16.1
ebonite	−20.3	−18.6
mica	−18.9	−15.3
crown glass	−19.2	−16.7
lead	−19.7	−17.0
para rubber	± 8.	± 5.

increased to 2 kg/cm², the charge rose to a maximum, and then remained constant for pressures up to 5 kg/cm². The quantities recorded in the table are the mean values of this maximum charge. Except when the two kinds of rubber were pressed against each other, the charge of the rubber was negative in every case. The results show that although the dielectric constants of the hard substances ranged from 2.8 for ebonite to 7.8 for flint glass, the charge of the compressible material remained approximately independent, both in sign and in magnitude, of the

nature of the material against which it was pressed. Since an electrification of this sort cannot be entirely a Volta effect, we may conclude that the greater portion of it is due either to the distortion of the surface of the compressible dielectric or to an internal distortion like that which produces the phenomenon of piezo-electricity. The second hypothesis does not seem probable; for, although the pure sheet contained a certain amount of crystalline sulphur, the para contained very little, if any; and inasmuch as the electrification is approximately 2000 times as large as that which is always associated with the formation of a new surface of a liquid,[18] the distortion of the surface does not seem adequate to account for the whole of the effect. There is nothing in the results, however, to preclude the possibility that a hitherto undescribed effect of compressing an amorphous material occurs in a degree large enough to mask both the surface and the Volta effects.

Effect of Collision

In a recent paper[5] it has been shown that a solid dielectric acquires a perfectly definite charge whenever it collides with a metal, provided the relative velocity of the two bodies exceeds a certain minimum value at the moment of contact. The quantity of electric energy produced in this manner was found to be independent of the amount of mechanical energy lost during the collision, and the conclusion was therefore drawn that electrification by impact is the true Volta effect of the colliding materials. The results of the present experiments, however, considered together with the data of electrification by collision, show that the latter can be due only in part to an intrinsic difference of potential. In particular, quartz, flint glass, crown glass, fluorite, calcite, ivory, and ebonite are all *negatively* charged by collision with steel, brass, or zinc; whereas the results given in Table III prove that the first four of these materials are consistently *positive* to steel in the true contact series. Here are four pairs of substances for which the effects of contact and collision, respectively, are oppositely directed. The difference of sign cannot be considered to prove that impact does not give rise to the Volta effect; for the results given in the earlier portions of this article show clearly that the collision of a polished glass sphere and a metal, at a relative velocity of 200 to 250 cm per sec., may be expected to produce a sufficiently intimate contact to establish the characteristic voltaic charge. We must therefore conclude that collision gives rise to two different effects, one of which is the contact electrification, while

[18] Nolan and Enright, Roy. Dublin Soc., Proc. **17**, p. 1, 1922.

the other is a transfer of electrons from the metal to the dielectric, due to the inertia of the mobile electrons. In the cases referred to here, the second of these effects was not only greater than the characteristic contact charge, but also approximately 200 times as large as the well known inertia effect discovered by Tolman and Stewart.[19] There is no conflict, however, with their results, for the rate of change of momentum occurring at the instant when an elastic sphere collides with a massive metal body, after having been projected vertically upwards with a moderately large velocity, is much greater than that which Tolman was able to produce in bringing his moving conductor to rest; and furthermore, the rate of change of momentum in the latter case was not important so long as the velocity was reduced to zero in a time sufficiently small to satisfy the requirement that the galvanometer used to detect the inertial effect should operate ballistically.

The discovery of the importance of the relative velocity of two bodies in determining the contact electrification shows that the e.m.f. of a voltaic cell may be expected to vary with the acceleration of the electrodes, as Professor Kleeman has recently suggested,[20] although his theory of the transition layer does not seem necessary to account for such an effect. The so-called anomalous behavior of mercury,[1] which becomes positively charged when struck with glass but negatively when rubbed with the same material, is also easily seen to be in accord with the present results; and numerous other discrepancies, usually attributed to the contamination of the surfaces of contact, may now be referred to the failure of experimenters to distinguish among the different electrifications which are due, respectively, to collision, to compression, and to the voltaic difference of potential. More accurate determinations of the constants of these effects, for a larger variety of materials, may be expected not only to furnish a single contact theory which will include both the metals and the dielectrics, but also to shed a good deal of light on the structural differences of these two kinds of matter.

The writer has the pleasure of thanking the National Research Council for the grant of a fellowship permitting him to carry on, without interruption, this and an ensuing study.

NATIONAL RESEARCH FELLOWSHIP,
PALMER PHYSICAL LABORATORY,
PRINCETON UNIVERSITY,
February 19, 1923.

[19] Tolman and Stewart, Phys. Rev. **8**, p. 97, 1916; also **9**, p. 164, 1917.
[20] Kleeman, Phys. Rev. **20**, p. 174, 1922.

EXPERIMENTS ON THE SIGN OF THE ELECTRIC CHARGE ASSUMED BY A METAL IMMERSED IN A LIQUID

By Richard D. Kleeman and William Fredrickson

Abstract

Electric charge assumed by various metals and carbon immersed in distilled water was determined by noting the direction of motion of clean wires suspended by a long silk thread, when an electric current was passed through the water in which they were immersed. It was found that *Ag, Al, Au, C, Cu, Mg, Mo, Ni, Pt, Sn, W, and Zn* acquired a negative charge while *Bi, Cd, Fe, and Pb* became positive.

Electric charge assumed by colloidal particles of Ag, Au, Bi, Fe, Pb, and Pt determined from their direction of motion in an electric field by other investigators, was found to agree with the results obtained with suspended wires. According to the *transition layer theory* of voltaic e. m. f. previously proposed, this charge is due to the segregation of +H and −OH ions in the layer next the plate as a result of the different rates of diffusion of the two ions.

THE nature of electric charge assumed by a metal plate immersed in a liquid is of importance in connection with the theory of the e.m.f. of a voltaic cell, the direction of motion of colloidal particles under the influence of an electric field, etc. The object of this paper is to describe a set of experiments on the charge assumed by various metals in distilled water.

The metal to be investigated was in the form of a very thin wire about 4 cm long which was attached to a silk thread about two metres long running along the axis of a vertical glass tube. About 3 cm of the wire were immersed in distilled water, which was contained in a tank with glass sides whose dimensions were $3\times4\times6$ cm. Two electrodes, usually aluminum corresponding in size to the two smaller sides of the tank and in contact with them, served for sending a current through the water. The passage of a direct current was usually attended by a deflection of the wire either in the direction the current was flowing, or in the opposite direction, which was observed by means of a microscope focussed on to the lower end of the wire. This deflection, which in magnitude was usually several times the thickness of the wire, would be mainly due to the electric charge on the wire with respect to the solution, the wire moving with the current when positively charged, and against the current when negatively charged. But a motion would also be impressed upon the w re

on account of a magnetic effect, this motion being in a direction such as to increase the energy in the magnetic field. Its direction would evidently be independent of the direction of the current. To differentiate the effect due to the electric charge on the wire from the magnetic effect, the current was sent in one direction and the deflection noted, then reversed and again the deflection noted. In one case the deflection is due to both effects acting in the same direction and in the other case due to their acting in opposite directions.

In order to obtain values which should be influenced as little as possible by any oxidation of the wire, contamination of its surface, or impurities in the water, the water was replaced by freshly distilled water and the wire and electrodes cleaned with fine sand paper before carrying out a set of measurements. The readings were then taken as soon as the apparatus was ready. The deflection would usually be stationary after the current had been flowing about half a minute, and a set of readings could usually, therefore, be taken in two or three minutes. In this manner it was found that the metals Ag, Al, Au, Cu, Mg, Mo, Ni, Pt, Sn, W, and Zn and also carbon become negatively charged, and the metals Bi, Cd, Fe, and Pb positively charged, in distilled water.

It should be mentioned that if the current was allowed to flow for some time, say five minutes or more, small bubbles of gas, probably of oxygen and hydrogen, would begin to form on the wire. This would decrease the extent of the deflection of the wire, but not its direction. This state of affairs was usually avoided by obtaining measurements before any sign of bubbles appeared. The foregoing result is of interest since the same thing would happen to metallic colloidal particles in a liquid through which a current is sent, and the change in velocity of the particles with time often observed may be well explained in this manner.

The metals Ag, Au, Bi, Fe, Pb, and Pt have been obtained in colloidal solution in water, and the directions of their motion under the action of an electric field have been observed. The results indicate that the metals Bi, Fe, and Pb are positively charged with respect to water, and the metals Ag, Au, and Pt negatively charged. This falls into line with the preceding results. It appears, therefore, that the process of obtaining the particles in colloidal solution does not change their surfaces, as it well might, to an extent which would reverse the sign of the charge.

It will be of interest to consider the results obtained in the light of a transition layer theory of the e. m. f. of a cell previously[1] proposed. According to this theory a liquid transition layer exists at the boundary of

[1] Kleeman, Phys. Rev. **20**, p. 174, 1922.

a plate immersed in a liquid, and this has an electric field across it due to a segregation of positive and negative ions. This gives rise to a charging up of the plate due to the motion of translation of the ions, the charge on the plate being the same as that of the ion existing in surplus near the plate. The direction of the electric field across the layer for a given liquid depends on the nature of the material of the plate. It appears therefore that in the case of the metals copper, tungsten, silver, molybdenum, magnesium, aluminium, carbon, nickel, gold, platinum, tin and zinc, immersed in distilled water, there is a surplus of $-OH$ over $+H$ ions in the part of the transition layer in the immediate vicinity of the plate, and in the case of the metals bismuth, lead, iron and cadmium, a surplus of $+H$ ions. This surplus is caused chiefly by the rate of diffusion of the negative ions towards a plate being greater than that of the positive in the case of the first set of metals, and the reverse being the case with the other set. The relative rates of diffusion of the two kinds of ions would be largely affected by the density and the polymerization gradients in the transition layer. The former gradient would depend largely on the density of the metal plate, and the latter gradient on its nature. Since the two sets of metals are not divided according to their densities, this seems to indicate that each set has a distinct catalytic effect on the polymerization of water molecules.

The oxidation of a metal in water is not caused by a surplus of $-OH$ over $+H$ ions in its vicinity, as will appear from an inspection of the foregoing two sets of metals. It is due to the presence of free oxygen, as is shown by the fact that a metal kept in distilled water in a closed tube from which the dissolved and occluded gases have been removed by boiling does not show any signs of oxidation.

We wish to express our thanks to the General Electric Company for supplying most of the wires used in these experiments.

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UNION COLLEGE, SCHENECTADY, N. Y.
February 8, 1923.

THE THERMOELECTRIC PROPERTIES OF SPUTTERED FILMS OF GOLD, PLATINUM, AND PALLADIUM; AND OF SOLID PALLADIUM CONTAINING OCCLUDED HYDROGEN

By R. M. Holmes

Abstract

Thermoelectric properties of sputtered films of gold, platinum and palladium.—The films were sputtered on glass in a tube containing air not specially dried, the desired shapes being secured by use of mica screens. One end of a film was kept at 0°C; the temperature of the other junction was varied by use of an electrically heated oil bath. For monometallic couples of Au, Pt and Pd, each consisting of a film in contact with its mother metal, surprisingly large electromotive forces were observed. For the unbaked films the power line shows breaks and the values decrease with time. If the films are baked at 500° C, however, the electromotive forces are definite though smaller and the power lines are straight, the values of $dE/d\theta$ for the baked films with respect to the mother metal for the range 0° to 300° C, increasing from −.90 to −1.23 for gold, and from 6.59 to 9.6 for Pd, and being constant at 3.46 for Pt, all in microvolts per degree. These values do not vary with the thickness, and agree with the results obtained with Pt film–Au film couples.

Effect of occluded hydrogen on the thermoelectric power of palladium was studied as it was thought that the peculiarities shown by the film couples might be due to occluded gas. The metal when filled with hydrogen electrolytically was found positive with respect to the gas-free metal, the value for $dE/d\theta$ decreasing from 12 microvolts per degree at 0° to zero at 270° C. When filled by cooling in hydrogen in a furnace, smaller values were obtained. Baking removed the effect. *Electron theory* in its simplest form, taking the thermoelectric power as proportional to the logarithm of the electronic pressure ratio, is shown to give a value for the gas-filled metal due to the effect of hydrogen in increasing the electronic pressure, which agrees approximately with the experimental value.

WHILE there is an extensive literature on the general subject of cathodically deposited films, their thermoelectric properties have never been studied. The purpose of this investigation was to compare the thermoelectric power of a film couple with that of the solid metals from which the films were sputtered. The results obtained suggested the investigation also of the effect of occluded hydrogen upon the thermoelectric properties of solid palladium.

Preparation of the Films

The films were deposited on glass strips by the ordinary method of cathodic sputtering. Briefly, a strip of metal (1×10 cm) was used as the cathode in a gas discharge within a bell jar containing air at a pressure

of about 0.01 mm and with a current density of from 0.00024 to 0.00042 amp. per cm² of cathode area. A glass strip upon which the film was to be deposited was placed under the cathode and just inside the boundary of the Crookes dark space. By use of a mica screen a film of any desired shape could be deposited. The thickness was regulated by the duration of the discharge.

In the first part of the work, platinum and gold films were sputtered to form a thermocouple. The metals used as cathodes were of a high degree of purity. One of the films was deposited while a screen kept the rest of the glass free from metal. The jar was then cleaned, the cathode changed, and the other film deposited, while another screen was used to confine the sputtered metal to the desired region on the glass strip. The films were deposited with overlapping ends as shown in Fig. 1. The width of the films was 0.6 cm and their length to the overlapping portion was 10 cm.

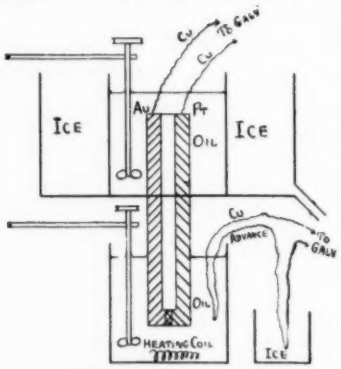

Fig. 1. Apparatus.

The apparatus for maintaining any desired temperature at the hot junction while the cold junction remained at 0°C, is shown in Fig. 1. The overlapping portions of the films were submerged in an oil bath which was heated by a resistance coil supplied with alternating current. As it was desirable to obtain temperatures as high as 300°C, several kinds of oil were tried and a high grade automobile oil was finally selected, which proved superior even to castor oil.

A length of about 4 cm of the films was submerged in the oil. A stirrer kept the oil at a uniform temperature which was determined by means of a calibrated copper-advance thermocouple. The other ends of the films were in an oil bath kept at approximately 0°C by surrounding it with an ice compartment. A clamp was used for establishing connections between the cold ends of the films and the galvanometer or potentiometer used for measuring the thermal e.m.f. On account of the rather small dimensions of the apparatus and the fairly large temperature differences it was necessary to provide good heat insulation.

Results with Platinum film-Gold film Thermocouples

The following is a list and description of the film thermocouples used in some preliminary experiments summarized below. Some couples

were baked in an electric oven while others had no heat treatment previous to their use. Thickness is described by appearance with transmitted light. No. 8 was heaviest of all the films being as thick as ordinary gold leaf.

Couple No.	Resistance	Heat Treatment	Thickness	Results
2	14.7 ohms	Baked at 500° C	Opaque	Fig. 4
7	62.5	None	Opaque	Fig. 2
8	19.0	None	Very Thick	Fig. 2
10	43.6	Baked at 350° C	Opaque	Fig. 4
12	181.0	None	Transparent	Fig. 2

These couples differ greatly from a couple consisting of the same metals in solid form. The film couples vary somewhat among themselves but the following are general characteristics applying to all:

(a) *Unbaked film couples* (Figs. 2 and 3). The platinum film is positive at the cold junction while with the solid metals gold is positive. Thermal

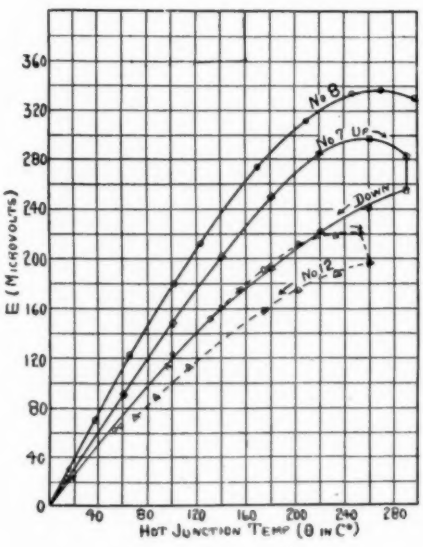

FIG. 2

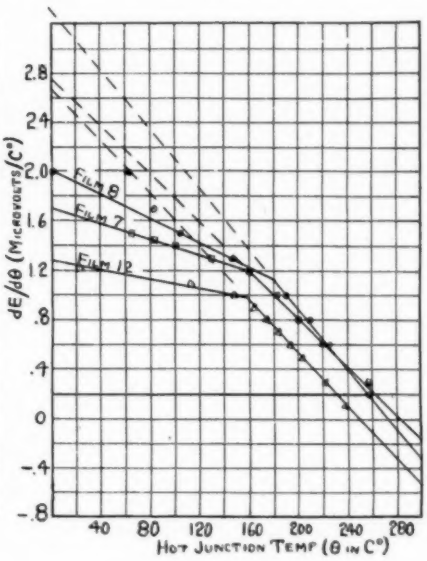

FIG. 3

Fig. 2. Thermal e.m.f. of Au-Pt film thermocouples (unbaked).
Fig. 3. Thermoelectric power of gold-platinum film thermocouples (unbaked).

e.m.f. decreases gradually with time at a steady hot junction temperature, thus causing the e.m.f. to be lower on descending temperatures. The e.m.f. of the film couple is much smaller than that of the solid metals for all hot junction temperatures. For example, at 200°C the film couple has an e.m.f. which is from 12 to 18 per cent of the solid metal

value. Other characteristics are: The thermoelectric power is not a linear function of hot junction temperature as is the case with the solid metals for this temperature range, and the neutral points (where $dE/d\theta = 0$) are located at temperatures much higher than -130°C, which is the neutral point for the strips of gold and platinum used in sputtering the films.

(b) *Baked film couples* (Fig. 4). When baked at 500°C, the polarity is the same as that of the mother metals. The thermal e.m.f. is still much lower. For example, at a hot junction temperature of 200°C it is 12 per cent of the solid metal value. Fig. 4 shows that after being

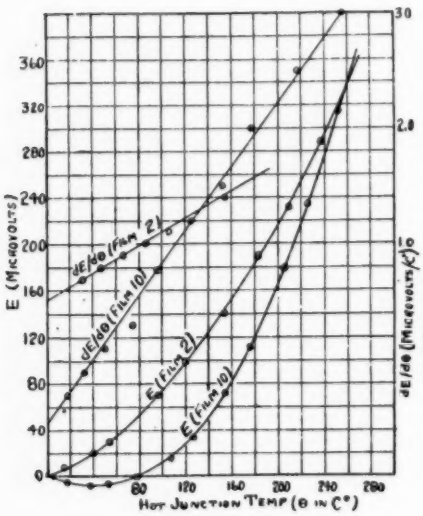

FIG. 4

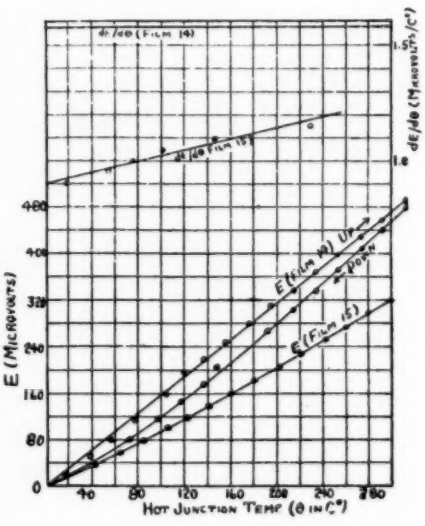

FIG. 5

Fig. 4. Thermal e.m.f. and thermoelectric power of Au-Pt film thermocouples (baked).
Fig. 5. Thermal e.m.f. and thermoelectric power of gold film-solid gold thermocouples. Film No. 14 (unbaked); Film No. 15 (baked).

baked at 500°C, the thermoelectric power of the film couple is a linear function of hot junction temperature, and the neutral point (located at about -90°C) is nearer the solid metal value than is the case with the unbaked films.

THERMOELECTRIC EFFECTS IN A MONOMETALLIC CIRCUIT CONSISTING OF SOLID METAL AND A FILM

The results obtained with film couples make it evident that a thermocouple may be made with solid metal for one element and the same metal in the form of a film for the other element. This point was

investigated with gold, platinum, and palladium. The films (1×10cm) were sputtered on glass. A narrow strip cut from the cathode used in sputtering the film was placed on the other side of the glass strip and the apparatus shown in Fig. 1 served to maintain the two junctions of film and solid metal at any desired temperature difference.

The following is a list of the films referred to in this connection.

Film	Resistance	Heat Treatment	Thickness	Results
Au No. 14	5.2 ohms	None	Opaque	Fig. 5
Au 15	3.2	Baked at 500° C	"	Fig. 5
Pt 28	48.	None	"	Fig. 6
Pt 28	22.	Baked at 500° C	"	Fig. 6
Pt 32	1400.	None	Transparent	——
Pt 50	217.	"	"	——
Pd 61	120.	"	Opaque	Fig. 7
Pd 62	31.	Baked at 500° C	"	Fig. 7

Film No. 28 was used both before and after baking. Film No. 32 was very thin. Film No. 50 was sputtered while hydrogen was being admitted to the sputtering jar.

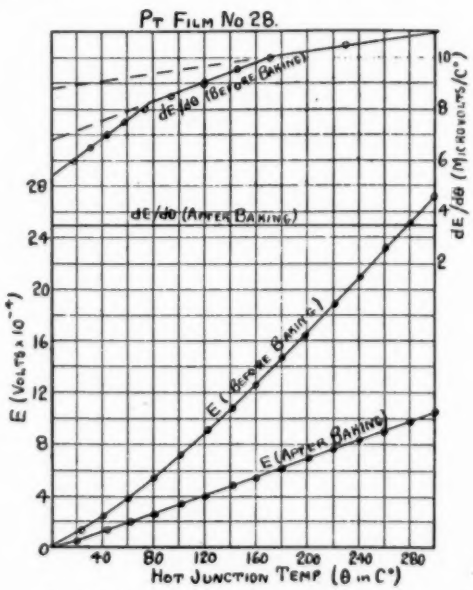

Fig. 6. Thermal e.m.f. and thermoelectric power for platinum film-solid platinum thermocouples (baked and unbaked).

The gold film is negative to the solid metal at the cold junction while platinum and palladium films are positive to their mother metals. Different films of any one of these metals give very nearly the same results. Thickness has no effect upon the thermoelectric properties

of a film, at least down to very thin films. This was proven by measurements on many films and is illustrated by the fact that the curves for films 28 and 32 practically coincide although the former was heavy while the latter was very thin. Also, it made no difference if the sputtering jar was first washed out with hydrogen and this gas slowly admitted during the deposition of the film and while the pumps were running. Sputtering on mica, on smooth glass and on ground glass gave the same results.

Heat treatment received during a determination of thermal e.m.f., so affects the *unbaked* platinum and palladium films that their thermal e.m.fs. can be represented for the whole temperature range only by a series of two or more parabolas. This was not detected in the case of gold. The *baked* films, however, are permanent, provided they are not used at a temperature above that at which they were baked. After being baked at 500°C the thermal e.m.fs. are represented by the following equations, where E is in microvolts and θ is the hot junction temperature.

For gold: $E=0.90\ \theta+0.0059\ \theta^2$.

For platinum: $E=3.46\ \theta$.

For palladium: $E=6.50\ \theta+0.00515\ \theta^2$.

The Effect of Absorbed Hydrogen on the Thermoelectric Properties of Solid Palladium

The experiments on the effect of absorbed hydrogen were tried because it was thought that the large thermal e.m.f.s. in the monometallic circuits of platinum and of palladium might be due to gas absorbed by the films during the sputtering process. Difference in crystalline structure between film and solid metal from which it was sputtered cannot account for the effect, since Kahler[1] found the same structure in both film and solid metal. His results showed that the sputtered particles leave the cathode in granular crystals, probably being knocked off by impinging gas ions. Under these conditions the small granules of platinum and those of palladium should absorb gas, especially hydrogen, if it is in the sputtering jar. Spectroscopic observations showed that hydrogen was always present while the films here described were being sputtered. It probably came from traces of water vapor.

Palladium is especially suitable for these experiments since it is well known to have the property of absorbing several hundred times its own volume of hydrogen. The sample of metal used was in the form of a strip $0.01\times0.125\times10$ cm. It was cut from the palladium cathode used

[1] H. Kahler, Phys. Rev., 18, p. 210, 1921.

in sputtering the films. The metal was of a fairly high degree of purity but contained traces of rhodium, iron, and platinum.

This strip of palladium was first annealed in a vacuum at 1000°C. Then its thermal e.m.f. against a strip of pure annealed platinum was obtained (see curve 1, Fig. 8). Palladium is negative to platinum at the cold junction. The strip was then heated (always in a vacuum) to 700°C and allowed to cool while surrounded with an atmosphere of hydrogen, to approximately room temperature. Palladium absorbs hydrogen under these conditions. The thermal e.m.f. of the gas-filled metal

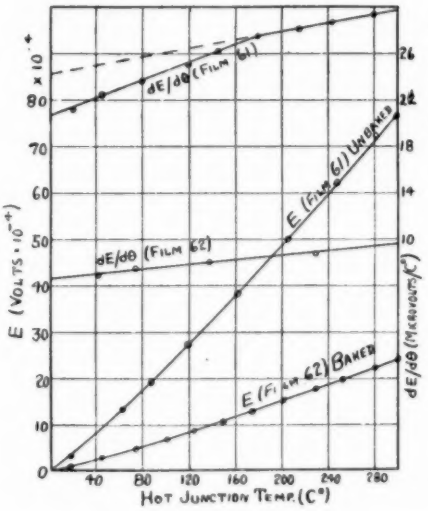

FIG. 7

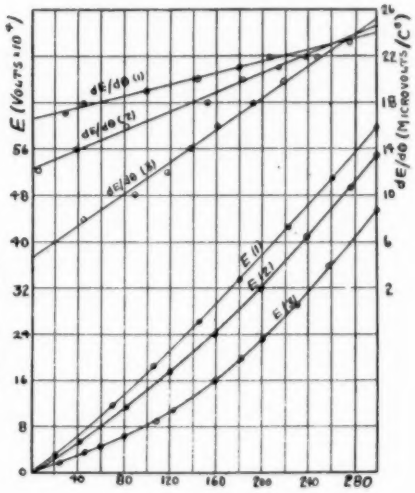

FIG. 8

Fig. 7. Thermal e.m.f. and thermoelectric power of palladium film-solid palladium thermocouples. Film No. 61 (unbaked). Film No. 62 (baked).

Fig. 8. Thermal e.m.f. and thermoelectric power of gas-filled and gas-free palladium against platinum. Curve 1, gas-free; Curve 2, furnace filled; Curve 3, electrolytically filled.

against platinum was determined (see curve 2, Fig. 8). Upon removal of the absorbed hydrogen by heating, the thermal e.m.fs. always returned to the original gas-free values. The following equations were obtained from the slopes of the curves.

For gas-free palladium against platinum:

$$E = 16.6\,\theta + 0.012\,\theta^2.$$

For palladium filled by cooling in an atmosphere of hydrogen:

$$E = 12.2\,\theta + 0.020\,\theta^2.$$

Both equations give E in microvolts, θ being the hot junction temperature while the cold junction is at 0°C.

The palladium strip was also filled with hydrogen by being used as the cathode in the electrolysis of a very dilute solution of sulphuric acid. It was allowed to absorb all it was capable of holding under these conditions and its thermal e.m.f. was determined against platinum (see curve 3, Fig. 8). Upon removal of the gas the results of curve 1

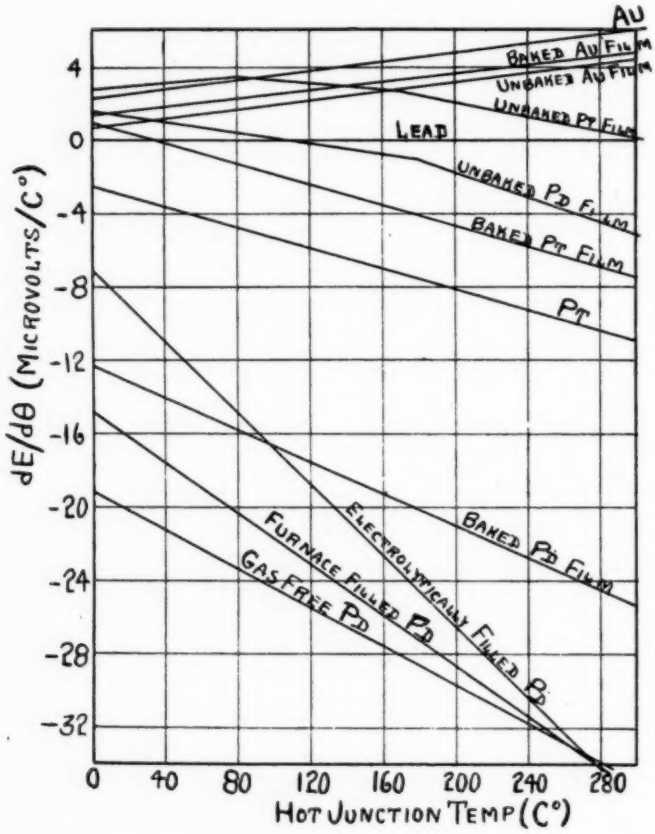

Fig. 9. Thermoelectric power referred to lead, for the films and solid metals and for palladium containing occluded hydrogen.

were again obtained. This process was repeated several times with perfectly consistent results. The following equation was obtained.

For palladium electrolytically filled with hydrogen:

$$E = 4.60\,\theta + 0.035\,\theta^2.$$

Summary and Discussion of Results

The diagram in Fig. 9 will serve to summarize and to clarify the results. Here the thermoelectric powers are referred to lead.

The effect of sputtering gold is to move the thermoelectric power line in the negative direction of the axis of ordinates, at the same time keeping it parallel to its original position. The fact that the line is moved parallel to itself shows, according to thermoelectric theory, that the Thomson coefficient has the same value in both film and solid metal. Baking the film partially restores the line to its original position. With platinum, sputtering moves the line in the positive direction and by a much larger amount than is the case with gold. The line is moved so far that, for a part of the temperature range, it is even above the line for solid gold, and for a greater part of the temperature range it is above the line for the unbaked gold film. Baking the platinum film moves the line toward the solid metal position. The line for a baked platinum film is parallel to the line for solid platinum, showing the equality of the Thomson effects in these two cases. When palladium is sputtered, the line is also moved in the positive direction and the shift is much greater than in the case of platinum. Here, also, the effect of baking is to make the film more like the mother metal in thermoelectric properties. The thermal e.m.fs. obtained in the monometallic circuits of platinum and of palladium are surprisingly large. In the case of palladium, this is believed to be the largest thermal e.m.f. ever recorded for a monometallic circuit.

The effect of absorbing hydrogen on bulk palladium is to move the line for this metal toward the position occupied by the sputtered film line. The line, however, is not moved parallel to itself but in the new position it comes, for the higher hot junction temperatures, into the region of the diagram occupied by the gas-free metal. This is because of the liberation of hydrogen by heat conducted from the hot junction along the region of the temperature gradient in the metal. For this reason the gas-filled strip becomes inhomogeneous, that part near the hot junction having a smaller gas content than the part which is more distant. The result is that error is introduced in the determination of the thermoelectric power from the slopes of the e.m.f. curve.

These results show that a monometallic circuit consisting of gas-free and gas-filled palladium will develop a thermal e.m.f., and that the gas-filled metal will be positive to the gas-free metal at the cold junction. The equation for the thermal e.m.f. in such a circuit may be obtained by subtracting the equation for the gas-filled palladium from the equation for the gas-free palladium, both against platinum as a reference metal. The equation obtained is:

$$E = 12.0\,\theta - 0.023\,\theta^2.$$

This effect of absorbed hydrogen upon bulk palladium favors the conclusion that absorbed gas is the principal cause of the thermal e.m.fs. obtained with platinum films and with palladium films used in thermocouples with their mother metals as the other elements. Gold would not be expected to show this effect because it is not a good gas absorber. The comparatively small effect found in gold is in the other direction and is probably due to other causes which may operate in the cases of the other metals but which are more than out-weighed by the effect of the absorbed gas.

Platinum films would be expected to show the effect in smaller measure than palladium films because the latter metal is known to be a much better absorber than the former. The experimental results agree with this deduction. Absorbed gas is expelled by baking, and likewise the thermal e.m.fs. in the platinum and in the palladium circuits are greatly reduced by baking the films. Platinum and palladium films sputtered while hydrogen was being admitted into the jar did not differ from those sputtered when no hydrogen was admitted. This would be due to the fact that there was always enough hydrogen (presumably from water vapor) in the jar to completely saturate the extremely small mass of metal deposited as a film. The fact that baking did not completely remove the thermal e.m.fs. in the film-solid metal circuits would indicate that gas is not as easily removed from the very small granules of a film as from bulk metal.

Application to the Electron Theory of Thermoelectricity

The electron theory furnishes the following expression for the thermoelectric power of any couple:[2]

$$dE/d\theta = (R/e) \log (p_2/p_1) \qquad (1)$$

where R and e are the gas constant and charge per electron and p_1 and p_2 are the electronic pressures in the two elements of the couple.

From this, qualitatively, one might predict that absorbed hydrogen would make palladium positive to the gas-free metal for two reasons. First, McKeehan[3] has recently shown that the hydrogen atoms actually penetrate inside the crystals of palladium and occupy positions between the palladium atoms. This would decrease the space available for free electrons if the expansion of the metal due to the occlusion of the gas were not enough to compensate for the effect. Second, the hydrogen may itself lose electrons, thus increasing the total number inside the gas-

[2] O. W. Richardson, Phil. Mag. **23**, p. 273, 1912.
[3] L. W. McKeehan, Phys. Rev., **20**, p. 82, 1922.

filled metal. Anderson[4] has recently shown that hydrogen desorbed from palladium is ionized.

In order to obtain an approximate value for the thermoelectric power due to the first cause, we may develop a very simple theory from which to calculate the ratios of the electronic pressures in the gas-filled and gas-free metal. Assuming that the electrons obey ordinary gas laws, we readily obtain the equation

$$dE/d\theta = 198 \log_{10} [a/(a+nr-7.44\ nC\ \cdot 10^{-24})] \qquad (2)$$

In this equation the constants R and e have been evaluated and common logarithms used. Here a represents the fraction of the whole volume of palladium which may be termed interatomic space and which we assume available for free electrons in the gas-free metal. The number of volumes of hydrogen occluded is n, and r is the expansion of unit volume of palladium due to the occlusion of unit volume of hydrogen. C is the number of molecules in unit volume of hydrogen and the constant is the actual volume of a hydrogen molecule.[5]

The value of a must be somewhat less than unity. Calculated for solid hydrogen at -260°C it amounts to about 0.8. Let us assume this value for palladium. According to Graham[6] the value of nr is 0.098 and that of n is 956, both at about 15°C. Substituting these values in Eq. 2 we have: $dE/d\theta = 9.7$ microvolts per degree at 15°C, while the value experimentally found is 11.4.

The calculated value of the thermoelectric power agrees with the experimental value far better than could be expected considering the nature of the assumptions made. The theory predicts the correct polarity and makes $dE/d\theta$ equal zero for the case where n equals zero, in agreement with experimental facts.

Instead of assuming a value for a and calculating the thermoelectric power, a might be taken as unknown and calculated from the observed thermoelectric power. If this is done a comes out equal to 0.7.

These results are believed to offer some confirmation of the general correctness of the electron theory of thermoelectricity.

In conclusion, the writer wishes to express his appreciation of the encouragement and inspiration he has constantly received from Professor F. K. Richtmyer who suggested the problem. He also wishes to acknowledge aid from the Rumford grant to Professor Richtmyer.

CORNELL UNIVERSITY,
DEPARTMENT OF PHYSICS,
February 9, 1923.

[4] P. Anderson, Chem. Soc. J., **121**, p. 1153, 1922.
[5] J. A. Crowther, "Ions, Electrons and Ionization Radiation" p. 287 (1922).
[6] Graham, Proc. Roy. Soc., **17**, p. 500, 1869.

THE REMOVAL OF THORIUM FROM THE SURFACE OF A THORIATED TUNGSTEN FILAMENT BY POSITIVE ION BOMBARDMENT

By K. H. Kingdon and Irving Langmuir

Abstract

Sputtering of thorium from the surface of a thoriated tungsten filament.—The method of measurement depends upon the fact that by suitable thermal treatment a layer of thorium one atom thick can be formed on the surface of the filament and that the electron emission of such a layer at 1500° K is 10^5 times that of the tungsten and decreases according to known laws with the amount of thorium sputtered off as a result of bombardment by positive ions. The tube used contained, besides the central thoriated filament which was cold during the sputtering, two other filaments used to emit the electrons needed to produce the positive ions by collision. The gas was introduced at a low pressure, 6 bars, and *the effect of argon, caesium, helium, hydrogen, neon, and mercury ions as a function of voltage and time* was studied. H ions produced no sputtering even up to 600 volts energy. Ar, Cs, Hg and Ne ions all started to sputter the thorium ions at about 50 volts energy. The number of impacting ions of 150 volts energy per sputtered thorium atom varied from 12 for Ar and Cs to 45 for Ne and 7000 for He. The amount of thorium sputtered at first did not increase linearly with the time, and the rate of sputtering was greater when 0.95 of the surface was covered with thorium than when it was completely covered. In explanation, it is suggested that the removal of thorium takes place around the edges of holes or depression in the thorium coating; that for the removal of the first few atoms, two successive impacts on the same thorium atom are necessary; and that the first impact depresses the atom from the surface while at the second impact the ion is reflected from this depressed atom and knocks off one of the surrounding thorium atoms. A computation of the energies involved seems to bear out this theory. In the case of He the sputtering is so slow that a different mechanism must be involved, perhaps radiation, as suggested by Thomson.

Penetration of helium positive rays into tungsten.—The occluded helium was recovered by heating to about 1800° K, and in some cases the number of helium atoms was found equal to over ten times the number of tungsten atoms in the surface.

Introduction

THE DISINTEGRATION of the cathode in an electric gas discharge tube by the impact of positive ions on its surface is a subject which received some considerable attention during the early years of research in gaseous conduction. The main results obtained have been summarized by Kohlschutter,[1] and J. J. Thomson.[2] It was found that for all ions the

[1] Kohlschutter, Jahrb. d. Radioaktivitat **9**, 355, 1912

[2] J. J. Thomson, Rays of Positive Electricity (1921) p. 171

rate of disintegration, or sputtering, increased with the energy of the ions, that is with the voltage across the tube—or more particularly with the cathode fall. For a cathode of platinum the rate of sputtering was found in general to increase with the mass of the ion. For a given ion, say argon, the rate of sputtering tended to be less the lighter the cathode material, and for this reason aluminum electrodes are usually employed in spectrum discharge tubes.

Experimental Method

The removal of thorium from the surface of a thoriated tungsten filament by the impact of positive ions is a special case of cathode sputtering, and one which is admirably suited to a precise examination of the mechanism of the disintegration process. Langmuir[3] has shown that by subjecting a tungsten filament containing a small percentage of thorium oxide to suitable thermal treatment it is possible to obtain a complete layer of thorium one atom deep over the surface of the tungsten. At a temperature of 1500°K the electron emission from this thorium surface is about 100,000 times that from an equal area of pure tungsten. Hence removal of thorium from the surface by ion bombardment or otherwise exposes the tungsten underneath and decreases the electron emission of the filament. The connection between the fraction of the surface covered by thorium and the electron emission has been studied in detail by Langmuir,[3] so that we have here an exceedingly delicate method for studying the removal of minute quantities of thorium from the surface.

Vacuum Tube

The type of tube finally adopted[4] is shown in Fig. 1. The center filament *a* was the one whose surface was bombarded: it was made of thoriated tungsten wire 0.0101 cm in diameter. The two outer filaments *b* were of tungsten 0.0127 cm in diameter. The filaments were all 10 cm long. They were enclosed in a cylindrical anode (*c*, *g*) made by vaporizing tungsten from *b* on to the glass walls of the container. Platinum wires sealed through the glass made contact with the vaporized surface. This surface was divided into three sections electrically insulated from each other by the action of the quartz rings *q* which prevented the vaporized tungsten from striking the glass between *c* and *g*. The vaporization was continued until the resistance between the two leads of each anode section was about 1000 ohms. The ends of the anode cylinder

[3] I. Langmuir, Phys. Rev. **20**, 107, 1922

[4] Kingdon and Langmuir, Phys. Rev. **20**, 108, (1922)

were partially closed by two nickel disks g', pierced with holes through which the filaments passed. These disks were connected to the anode sections g. Their function was to prevent positive ions striking the leads of a, so that the entire ion current measured by a galvanometer connected to a was made up of ions which actually impacted on the center filament. The combination of g' and g will be referred to as g hereafter.

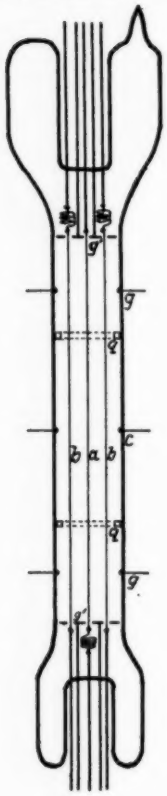

Fig. 1

It will be seen from the above that the construction of the tube was such as to avoid the presence of gaseous impurities. The tube was of lead glass, and was baked out at 360°C during exhaust. The nickel disks were glowed out by high frequency induction, the filaments were flashed, and tungsten was vaporized on to the glass to form the anode. The tube was then filled to about 6 bars pressure with the desired gas, and sealed off from the pump. During measurements the tube was immersed in liquid air up to the upper disks to get rid of the effects of water vapor on the thorium surface. Under these conditions the maximum thoriated electron emission from a was constant and reproducible.

The object of making the anode in three sections was to get rid of end effects; c and g were always kept at the same potential, but the electron emission from the center part of a to c could be measured alone. In this way a part of a could be studied which was at a uniform temperature, and over which impacting ions were distributed uniformly.

The b filaments were connected in parallel and heated so as to emit electrons, which were collected by c and g. This electron current produced ions by collision in the gas, and these ions were accelerated toward a by putting it at any desired negative potential with respect to b.

Let i_{ac} = electron current from a to c;

V_{ca} = voltage of c with respect to a;

i_a = ion current to a;

and let i_{bc} i_{bg}, V_{ab}, V_{cb}, etc. have similar meanings.

V_{cb} was always equal to V_{gb}, and was made as small as possible compared with V_{ab}, so as to give all the ions accelerated on to a as nearly as possible the same energy. i_{bc} and $(i_{bc}+i_{bg})$ were measured, and the total ion current i_a. The fraction of the ion current striking the center part of a was taken to be $i_a i_{bc}/(i_{bc}+i_{bg})$.

The experimental procedure consisted in bombarding a when cold with a known ion current for a short time; then heating a to a standard testing temperature (usually 1500°K) and measuring i_{ac}. This process was repeated until the emission from the center part of a had been reduced to any desired value owing to the removal of thorium. By plotting times of bombardment against corresponding values of i_{ac} a picture could be made of the rate of removal of thorium from the surface. Probably tungsten was sputtered also, but this made no change in the emission.

Experimental Results

The sputtering or deactivating effects of neon ions were studied in greatest detail, and will be discussed first. Fig. 2 shows two typical

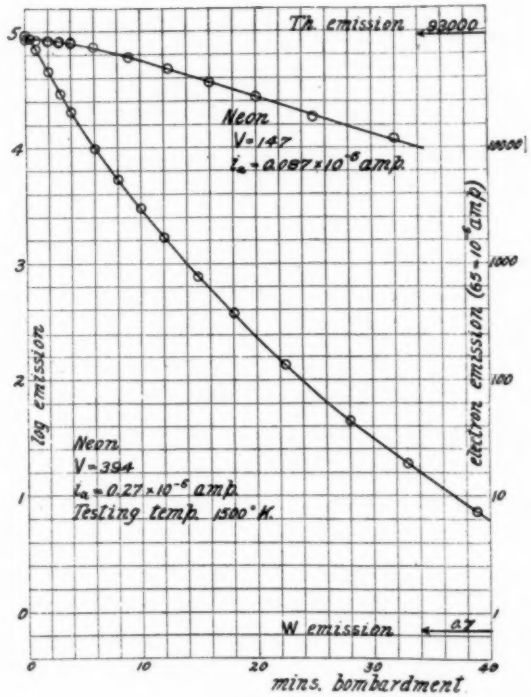

Fig. 2

deactivation runs; the ordinates are logarithms of i_{ac}, and the abscissae, times of bombardment. If we denote the fraction of the surface of a covered with thorium by θ, and the corresponding electron emission from such a surface by i_θ, Langmuir[3] has shown that when we pass from $\theta = 1$ to $\theta = \theta$ the electron emission changes in such a way that $\log i_1/i_\theta$ is pro-

portional to $(1-\theta)$. The initial emission in Fig. 2 is that characteristic of a thorium surface ($\theta=1$), while the arrow at the bottom indicates the emission characteristic of a similar tungsten surface ($\theta=0$). Since the ordinates are the logarithms of the currents the distance measured down on the ordinate axis is proportional to the fraction of the surface cleared of thorium, $(1-\theta)$. We are thus able to express unit distance on this axis in terms of the removal of a definite number of thorium atoms.

The center section of a was 4.85 cm long, and its surface area was 0.153 cm^2. The number of atoms per cm^2 of a tungsten surface estimated from the density is about 1.5×10^{15}. It seems most likely that a monatomic layer of thorium on tungsten has about half this number of atoms, or 0.75×10^{15} per cm^2. Hence there were 1.16×10^{14} thorium atoms on the surface of the center section of a. The ratio of the emission from a thorium surface to that from a pure tungsten surface at 1500°K was found to be 133,000, and the logarithm of this ratio is 5.12. Hence when the emission decreases to 1/10 of the maximum we have uncovered 1/5.12 or 19.5 per cent of the surface. This corresponds to the removal of 2.26×10^{13} atoms of thorium.

It was expected that the rate of removal of thorium would be proportional to the amount of it on the surface; that is, it was expected that the deactivation curves in Fig. 2 would start steeply, and gradually decrease in slope as the emission approached the pure tungsten value. The observed curves differ from this in not starting steeply but having a flat part at the top (see especially upper curve, Fig. 2), after which the rate of deactivation reaches a maximum value which is nearly constant over a considerable range of θ, and then decreases as the pure tungsten emission is approached. In order to explain this initial lag in the curve it was found necessary to formulate a somewhat novel theory of the mechanism of cathode sputtering, which will be discussed later. It is worth noting that when the thorium layer is removed by ordinary thermal evaporation there is no initial lag in the deactivation curve.

The deactivation curves obtained for argon, mercury, and caesium were similar to those for neon, and the mechanism of sputtering is probably the same for all these gases. Hydrogen ions had no deactivating effect up to 600 volts energy. Helium behaved in a different way from the other gases and will be discussed separately.

Deactivation curves were taken for neon at several values of the voltage ($V=V_{cb}+V_{ab}$) accelerating the bombarding ions. The slopes of the straight parts of the curves in Fig. 2 were taken as the basis for comparing the rates of deactivation at different voltages. From these slopes the ratio of the number of atoms removed to the number of ions

impacting on the filament could be found; this ratio is denoted by n. At the same voltage, the value of n was found to be approximately independent of the magnitude of the ion current, but most of the measurements were made at the same ion current so as to secure the best basis for determining the voltage variation of the rate of deactivation.

Fig. 3 shows values of n for neon, argon, mercury and caesium plotted as a function of the bombarding voltage. The values of n for helium

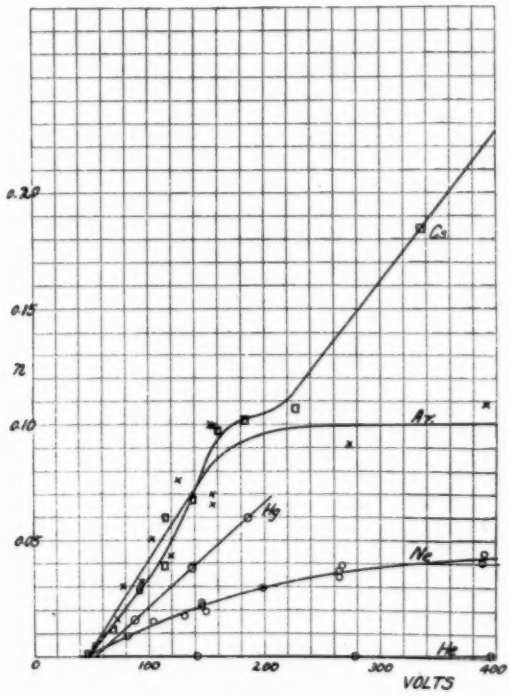

Fig. 3

plotted on the same scale are indistinguishable from the axis of abscissae up to 400 volts. There was some uncertainty in the experiments with argon, the points lying arbitrarily on one or the other of two straight lines, apparently independently of any known variation in the experimental conditions. The rate of removal of thorium falls to zero for all the gases at about 50 volts, a fact which is of considerable significance in connection with the theory to be described later. The values of the threshold voltage (V_0) required to start this sputtering as found from larger scale plots, and values of n at 150 volts are given in Table I.

Thus in the case of neon ions of 150 volts energy, only one ion out of 45 succeeds in removing a thorium atom from the surface.

The filament can be brought into the state in which a fraction θ of the surface is covered with thorium by three methods:

(1) thermal activation from $\theta=0$, (diffusion to surface);

(2) thermal deactivation from $\theta=1$, (evaporation from surface);

(3) positive ion deactivation from $\theta=1$ (sputtering).

Experiments were made to compare the rates of positive ion deactivation at $\theta=0.8$ after the surface had been brought to this condition by each

TABLE I

Sputtering data for various gases

V_0 = Threshold voltage for sputtering
n = Ratio of number of thorium atoms removed to number of ions (of 150 volts energy) impacting on filament.

Ion	V_0 (obs.)	V_0 (calc.)	n at 150 volts
H	>600	527	0.000
Ne	45	40	0.023
Ar	47	35	0.080
Cs	52	129	0.084
Hg	55	1600	0.044
He	(about) 35	142	0.00015

of these three methods. The rate of deactivation was the same after treatments (1) and (2), but was considerably slower after (3). This probably indicates that (3) produced a different distribution of thorium on the surface from that given by (1) and (2) for the same θ, and is of interest in connection with the mechanism of positive ion deactivation discussed later.

THEORETICAL DISCUSSION

Let us now discuss *the mechanism of cathode sputtering*, endeavoring in particular to explain the unexpected shape of the deactivation curves, and the fact that for argon, caesium, mercury and neon ions there exists a practically common threshold sputtering voltage of about 50 below which these ions are unable to remove thorium from the filament.

A neon ion impacting on a thorium surface with high velocity will drive the thorium atom which it strikes into the surface, but will be reflected itself and fly off.

The first result of the bombardment is therefore to produce a large number of depressions of atomic size in the surface of the filament. After a time a second atom will impact at the bottom of one of these depressions and be reflected from the thorium atom there. We must now decide whether this collision can be considered elastic; that is, whether the neon ion will retain a considerable part of its energy after reflection.

In the case of the impact of a gas atom with its velocity of thermal agitation on a surface, Langmuir[5] has shown that the energy given to the surface atom is transmitted so rapidly to neighboring atoms that the gas atom loses a large part of its energy, the collisions thus being in general inelastic. In the case of ion bombardment however, the velocity of the neon ions at the voltages used is 50 or 100 times greater than that of a neon atom at 300°K. The ion accordingly penetrates farther into the thorium atom and meets with much stronger fields of force, so that the time taken for reflection will be much shorter and the opportunity for dissipation of energy correspondingly reduced. It therefore seems justifiable to assume that neon ions may be reflected from thorium atoms and still retain a considerable part of their energy.

From these considerations we see that a neon ion which impacts on a thorium atom at the bottom of a depression in the surface probably will be reflected elastically, and on the way out may have enough momentum to knock off one of the surface thorium atoms around the edge of the depression. The first ion which drove the thorium down is reflected at the surface and so is not in a position to knock off any thorium. The removal of thorium therefore does not start until two or more ions have impacted in the same place on the surface; the first one makes a depression, and the second one is reflected from the bottom of the depression and may remove one of the atoms around its edge. This idea accounts satisfactorily for the initial flat part of the deactivation curve as will be seen from the following rough calculation, made for the case when θ is nearly unity.

Let p be the probability that the first neon ion impacting on the filament shall strike a selected thorium atom in such a way as to depress it below the surface, provided the ion has sufficient energy. If ν is the number of thorium atoms on the center section of a, it is obvious that p is of the order $1/\nu$; and it is to be expected that as the neon ion is smaller than the thorium atom p will be less than $1/\nu$.

Also let N be the number of neon ions impacting on the center section of filament a in time t. The probability that the same surface atom shall be struck *just twice* during the time taken for N ions to impact on the surface is, from the ordinary theory, $P_2 = \frac{1}{2}(Np)^2 e^{-Np}$. Although we have no detailed knowledge of the arrangement of thorium on the surface it seems safe to assume that a selected atom (atom 1) will be surrounded by four others (atoms 2, 3, 4, 5) which are the closest to it of any, and are approximately equidistant from it. We wish to calculate

[5] I. Langmuir, Journ. Am. Chem. Soc. **38**, 2221, (1916)

the probability that during the impact of N ions on the surface atom 1 shall be depressed, and that ions reflected from the bottom of this depression shall remove one or more of atoms 2, 3, 4, 5 around its edge.

Approximate calculation shows that on the average before the second ion impacts on 1, one of atoms 2, 3, 4, 5 will have been depressed in a manner similar to 1. There are thus three atoms left around the edge of the depression left by atom 1; and if μ is the chance that the ion reflected from depressed atom 1 shall remove a selected one of these three, the total chance of removing any one is 3μ. Accordingly $3\mu P_2$ gives the probability of removing an atom by the second of a group of two impacts on atom 1, occurring during N impacts on the whole filament.

We must also take into account the probabilities P_3, P_4, P_5 . . . that atom 1 shall be hit *just* 3, 4, 5 . . . times during the N impacts. Groups of more than 5 impacts are negligible under the experimental conditions. Considerations similar to those advanced above show that the total chances of removing atoms for these groups are respectively $5\mu P_3$, $6\mu P_4$, $6\mu P_5$ on the average.

The total chance of removing an atom of thorium by impacts on atom 1 is a measure of the fraction of the surface $(1-\theta)$ bared of thorium, and is given by

$$(1-\theta)=\mu(3P_2+5P_3+6P_4+6P_5) \tag{1}$$

Fig. 4 shows two deactivation runs which were made at very low rates of deactivation so as to be able to compare the initial parts of the curves with the values of $(1-\theta)$ calculated from (1). The circles represent the observations, and the curves were plotted from (1) using

$$\begin{cases}\mu=0.0268\\ p=1/2.6\times10^{14}=3.84\times10^{-15}\end{cases}$$

The number of thorium atoms ν on the surface of the center part of a was 1.16×10^{14}. By definition μ must be very much less than unity; and as pointed out above p should be of the order of magnitude $1/\nu$. It will be seen that the values found satisfy these conditions, and that the theoretical curve agrees well with the experimental data for the first 4 per cent of the surface uncovered.

These theoretical considerations support the view that the removal of thorium starts from around the edges of depressions or holes in the thorium coating. As the deactivation proceeds these holes become larger as thorium is removed from around their edges. It was noted above that at a given value of θ the rate of positive ion deactivation was greater when this value of θ had been produced by thermal treatment than when it had been reached by positive ion bombardment. This dif-

ference is probably to be ascribed to differences in the sizes of the holes in the surface produced by the two treatments.

More evidence in support of the theory is given by the minimum deactivating potentials (V_0) of Table I. Let us determine the energy interchanges involved at (a) the reflection of an ion from the atom at the bottom of a depression on the surface, and (b) the collision of the reflected ion with a surface atom.

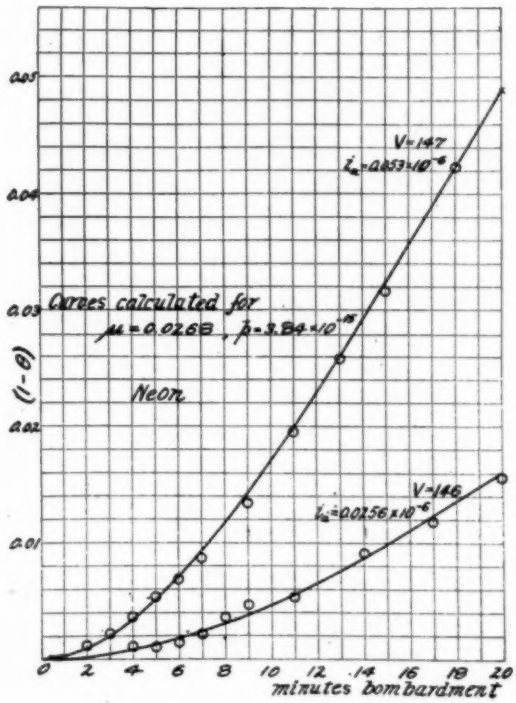

Fig. 4

(a) Let m_g and m_c denote the masses of the ion and cathode atoms respectively, and u_{g1} and u_{g2} the velocities of the ion before and after reflection, u_{c1} and u_{c2} being the corresponding velocities for the cathode atom. As a first approximation consider the collision to be between a free atom and a free ion, and neglect u_{c1}. The conservation of momentum gives

$$m_c u_{c2} = m_g(u_{g1} - u_{g2}) \tag{2}$$

and the conservation of energy gives

$$m_c u_{c2}^2 = m_g(u_{g1}^2 - u_{g2}^2) \tag{3}$$

From (2) and (3)

$$u_{g2} = u_{g1}(m_g - m_c)/(m_g + m_c) \tag{4}$$

(b) The neon ion after reflection impacts with velocity u_{g2} on a surface atom. Treating this collision similarly, but using v instead of u, that is putting $u_{g2}=v_{g1}$ we find

$$v_{c2}=2u_{g1}m_g(m_g-m_c)/(m_g+m_c)^2 \tag{5}$$

or for the energy of the cathode atom after the second collision

$$E=\tfrac{1}{2}m_cv_c^2=2m_cu_{g1}^2m_g^2(m_g-m_c)^2/(m_g+m_c)^4 \tag{6}$$

If V is the voltage through which the ion has fallen we have

$$u_{g1}=\sqrt{2eV/300m_g} \tag{7}$$

Substituting (7) in (6)

$$E=\left(\frac{4eV}{300}\right)m_cm_g\left[\frac{m_g-m_c}{(m_g+m_c)^2}\right]^2 \tag{8}$$

For the cathode atom to escape from the surface the energy given to it E must be greater than the atomic heat of vaporization. Langmuir[6] has shown that if ν is the number of gram-atoms of thorium evaporating per sec. per cm², from the surface of a thoriated tungsten filament

$$\log_{10}\nu=7.76-44500/T$$

Hence the slope of a plot of $\log_e \nu$ against $1/T$ would be 2.3×44500. From Van't Hoff's equation the heat of vaporization of thorium from tungsten is, therefore, $2.3\times44500\times R=203000$ gm cals. per gm mol., or 1.40×10^{-11} ergs per atom. This atomic heat of evaporation expressed as volts through which an electronic charge must fall to acquire an equal amount of energy is 8.8 volts.

For the case of neon ions and a thoriated tungsten cathode

$$E=0.220\,eV/300$$

Hence the threshold sputtering voltage V_0 should be given by

$$0.220\,eV_0/300=8.8e/300$$

or $V_0=40$ volts.

In a similar way values of V_0 for the other io ıs used may be calculated. Table I gives a comparison of the calculated and observed values of V_0 for all the gases used. For neon and argon the agreement is fair, considering the very approximate nature of the calculation. The values calculated for caesium and mercury are much too high. This is probably because in cases where the mass of the ion is comparable with that of thorium the thorium atom is driven far into the surface by the first ion striking it, and when the second ion strikes this depressed atom the collision cannot be considered to take place between a free ion and a free atom, but rather between an ion and a rigid wall. The ion therefore

[6] I. Langmuir, Phys. Rev. **20**, 107 (1922). The equation given in this paper for ν refers to gram-atoms per cm² per sec., instead of atoms.

would keep more of its energy on reflection than found in the above calculation, and be able to remove a surface atom at lower values of V.

As was mentioned before, *helium* behaved differently from the other gases used. In the first place it was found that relatively large quantities of helium penetrated into filament a during the bombardment and remained there. This helium could be recovered by heating a to about 1800°K for a minute or two. The number of helium atoms occluded in this way was in some cases equal to the number of tungsten atoms in the first 13 atomic layers of the filament. This means that the helium must have penetrated very deeply.

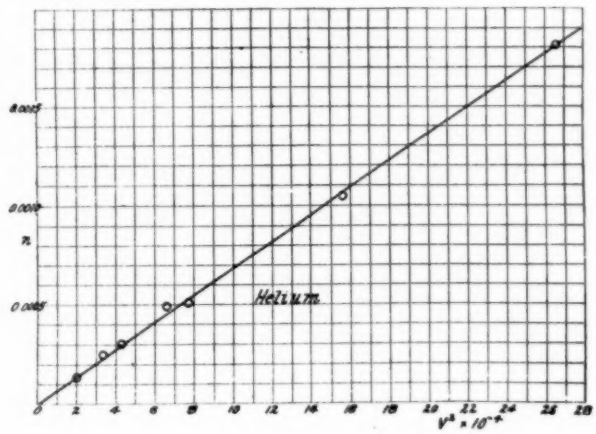

Fig. 5

In the second place as seen from Table I, helium ions could remove thorium from a at voltages much lower than those calculated from the theory. There is no reasonable explanation of this discrepancy here as there was in the case of caesium and mercury.

The rate of removal of thorium by helium was very small, being at 150 volts only 1/150 of that found for neon. The rate of removal increased proportionally to V^2 as shown in Fig. 5.

These facts find a possible explanation in a theory of cathode sputtering advanced by J. J. Thomson.[7] He suggested that the impacting ions cause radiation when they are stopped by the cathode; that this radiation is absorbed by the atoms on the surface in somewhat the same way as the electrons in an atom absorb resonance radiation; and that an atom may absorb enough energy to cause its ejection from the surface. The radiation emitted by an accelerated charge will on the classical theory increase rapidly with the acceleration. The helium ions penetrate into the fila-

[7] J. J. Thomson, Rays of Positive Electricity (1921) p. 176

ment and must be subjected there to accelerations which are enormous compared to those experienced by an ion which is stopped outside the surface. It is therefore reasonable that radiation may play an important rôle in the deactivation by helium ions, and not do so in that by neon ions, which apparently do not penetrate into the filament.

The intensity of heterogeneous x-ray radiation increases with the square of the voltage accelerating the bombarding electrons. We have seen that the rate of souttering of thorium by helium follows the same law. The radiation hypothesis also offers an explanation of why the deactivation continues to lower voltages than the limit of 142 given in Table I.

No attempt was made to detect any radiation given off by the bombarded filament, so the radiation theory remains merely a possible explanation of the observations.

RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY
SCHENECTADY, N. Y.
February 9, 1923.

THE COEFFICIENTS OF VISCOSITY AND SLIP OF CARBON DIOXIDE BY THE OIL DROP METHOD AND THE LAW OF MOTION OF AN OIL DROP IN CARBON DIOXIDE, OXYGEN, AND HELIUM, AT LOW PRESSURES

By James M. Eglin

Abstract

Coefficient of viscosity for carbon dioxide, determined by the oil drop method, was found to be 1.478×10^{-4} for 23° C and 76 cm pressure. This agrees well with Van Dyke's value 1.472×10^{-4} obtained by the constant deflection method. The constant A in the modified form of Stokes' law came out 0.815.

Motion of oil droplets in carbon dioxide, oxygen, and helium, at low pressures.—Measurements in these gases were extended to pressures of 1.9, 2.0, and 10 mm respectively, and to values of l/a, ratio of mean free path to oil drop radius, of 76, 130, and 71, respectively. The empirical correction factor to Stokes' law suggested by Knudsen and by Millikan, viz. $f(l/a) = 1+(l/a)\ (A+Be^{-Ca/l})$ was found to hold for all. Moreover the value of $(A+B)$ comes out the same for all within the experimental error, and equal to 1.175. The gases were carefully purified. A new atomizer for use at these low pressures was developed; otherwise the apparatus and methods were the same as those used by Ishida. *Comparison with motion of large ions.* The formulas of Lenard and Langevin for large ions are both the same as the empirical law for droplets, but the Wellisch formula cannot be extended to droplets whose mass is large with respect to the mass of a molecule.

IF the values of the elementary electrical charge and of the viscosity of air are assumed to be known, it is possible to obtain the coefficients of viscosity and slip of other gases by taking data on oil drops suspended in them. The theory and previous experimental results on various gases have been given in articles by R. A. Millikan, W. H. Barber, and Y. Ishida[1] for hydrogen; by L. J. Lassalle[2] for carbon dioxide; and by Y. Ishida[3] for hydrogen, helium, argon, carbon dioxide, methane, nitrous oxide, isobutane, and ethane.

I. Observations with Carbon Dioxide

The apparatus used for the work on viscosity and slip was the same as that used by Dr. Ishida. The carbon dioxide was prepared by heating

[1] Millikan, Barber and Ishida, Phys. Rev. **5**, 334, 1915.
[2] Lassalle, Phys. Rev. **17**, 354, 1921.
[3] Ishida, Phys. Rev. **21**, 550, 1923.

sodium bicarbonate, was passed through drying tubes, and condensed in a liquid air trap. Any small residue of air or other volatile gas was then pumped off. The liquid air was then replaced by a freezing mixture of salt and ice. The first and last portions of the carbon dioxide coming off were discarded. The vacuum system in which data were taken was evacuated to 0.05 mm before passing in the gas.

The other precautions taken, the method of determination of constants, and other details of procedure were the same as in previous work. A chronoscope was used to take the times of fall and rise of the drops.

The temperature of the surrounding oil bath was read on a Beckmann thermometer calibrated against a standard Baudin thermometer. The pressure was read on a good closed mercury manometer. The pressure was corrected to cm of mercury at 0°C and $1/pa$ was reduced to 23° C to make it proportional to l/a. The density of the oil was measured as 0.9298 and corrected for change of temperature by means of the formula $\sigma=0.9298-0.001AT$. f/η was reduced to 23° C by using the equation

$$(f/\eta)_{23}=(f/\eta)_t\ [535.8/(512.8+t)]\ (273.1+t)^{3/2}/(296.1)^{3/2}$$

This was obtained by putting $C=239.7$ in Sutherland's equation for the change of viscosity with temperature. For finding the voltage, an electrostatic voltmeter (range 200 to 900 volts) was used, the banks of small storage cells being divided into groups of three or four trays each (480 or 640 volts); and at the end of each day's run, the electrostatic voltmeter was compared at these voltages with a standard Weston electromagnetic instrument.

Data on forty-seven oil drops were obtained. Some of the drops traversed the scale approximately a centimeter in length, in about five seconds under the influence of gravity alone, while others took as long as fifty seconds. The variation in $(v_1+v_2)_0$ was only fourfold, from 0.003 to 0.012, but the number of charges n on the drops took on nearly all values between 2 and 90, the lower values being the more common. The drops were all large compared to those used in the later low pressure work, being from 1 to 4×10^{-4} cm in radius. The error in applying Stokes' law uncorrected would have been 1.9 per cent for drop number 1, and 22 per cent for drop number 47.

Some of the data on individual representative drops are given in Table I; all the results for f/η and for f, and the lines obtained from all the points by the method of least squares are given in Figs. 1 and 2. The intercept in Fig. 1 is 6765. This is equal to $1/\eta$, hence $\eta=1.478\times10^{-4}$ c.g.s. units. The values of the viscosity of carbon dioxide (at 23° C) previously obtained by this method are: by Lassalle, 1.490×10^{-4}; by Ishida 1.472

$\times 10^{-4}$. K. S. Van Dyke,[4] using the constant deflection or rotating cylinder method at about the same time that the present work was done found 1.472×10^{-4}. If we reduce Breitenbach's[5] result by assuming his viscosity for carbon dioxide too high in the same ratio as his value for ai probably is, it becomes 1.464×10^{-4}.

The accuracy of determination of coefficients of viscosity is probably less, and the labor much greater, for the oil-drop method than for the rotating cylinder method, though it may be possible, by using higher pressures, bigger drops, and consequently larger voltages, to increase the accuracy of viscosity determinations by the oil-drop method until its

TABLE I

Viscosity and slip of carbon dioxide

v_1	$(v_1+v_2)_0$	n	a	p	$1/pa$	$1/a$	f/η	f
.0223	.00290	76–81	40.15	39.89	62.9	.0295	6893	1.019
.0957	.00525	19–34	26.18	44.84	85.8	.0403	6920	1.023
.0714	.00593	12–25	22.03	46.20	98.7	.0463	7115	1.052
.0249	.00891	3– 7	13.08	46.42	165.4	.0776	7201	1.064
.0831	.00542	16–25	23.81	22.39	188.1	.0883	7239	1.070
.0730	.00559	13–24	22.34	22.43	201.1	.0944	7279	1.076
.0468	.00711	8–11	16.12	23.12	268.9	.1262	7511	1.110
.0289	.00949	5–16	13.67	22.29	329.7	.1547	7634	1.128
.0448	.00620	7–16	16.87	14.75	403.7	.1895	7776	1.149
.0358	.00723	5–28	14.90	14.74	457.0	.2145	7946	1.174
.0294	.00599	5–23	13.41	14.53	515.8	.2421	8122	1.200
.0348	.00706	6–10	15.47	11.23	578.0	.2713	8210	1.213

results are as reliable as those obtained by the constant deflection method. If constant conditions can be obtained at low pressures, the rotating cylinder method also makes the determination of the coefficient of slip much easier. The only advantage that the oil-drop method has over the other method is that since pressures of 10 cm and over may be used, trouble with occluded gases may be avoided, while with the other apparatus it is necessary to go to low pressures of the order of 0.3 mm or less.

The relation of l to $1/p$ is obtained from

$$\frac{l_c}{l_a} = \frac{(\eta/\rho u)_c}{(\eta/\rho u)_a} = \frac{\eta_c}{\eta_a}\sqrt{\frac{\rho_a}{\rho_c}}$$

and from $l_a = 7.156 \times 10^{-4}/p$ as used by Millikan[6] in his evaluation of e, the subscripts a and c in the first equation referring to air and to carbon dioxide respectively. The value of the slope obtained by plotting

[4] Van Dyke, Phys. Rev. **21**, 250, 1923.

[5] Breitenbach, Ann. der Phys. **5**, 166, 1901.

[6] Millikan "The Electron."

$f(l/a)$ against l/a (Fig. 2) is 0.815. Hence A the constant in the correction term of Stokes' law, is 0.815. Lassalle obtained 0.825, Ishida 0.84, and Van Dyke's value, determined subsequently, was 0.83. These results indicate that the slip constant (which is proportional to A) for carbon dioxide and oil is less than that for air and oil, since A for air and oil was found to be 0.86 by Millikan and also by Ishida.

II. The Law of Motion at Low Pressures

The linear relation $f(l/a)=1+Al/a$ for the correction term to Stokes' law breaks down at $l/a=0.4$ or above. This was found by Millikan and

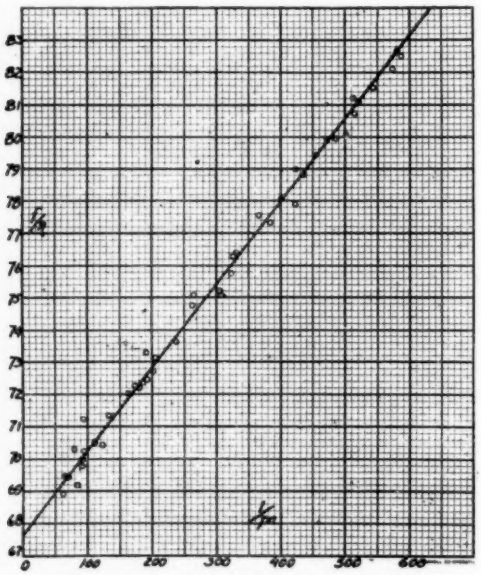

Fig. 1. Viscosity observations for CO_2; f/η as a function of $1/pa$.

by Knudsen[7] to be true for air, and the formula was extended empirically to $1+l/a\ (A+Be^{-Ca/l})$, where A, B, and C are constants. It was desired to test this relation for other gases.

Purification of gases. The gases were always approximately saturated with the vapor of the watch oil of which the drops were formed. The process of purifying the carbon dioxide has already been described. Oxygen was at first made by the electrolytic method, but the resulting gas contained so much hydrogen that its viscosity was markedly affected, and the rate of yield of gas was also slow. A better method consisted in heating potassium permanganate. The gas issuing from the generat-

[7] Knudsen, Ann. Phys. **36**, 981, 1911.

ing flask was passed through a liquid air trap, phosphorus pentoxide tubes, and another liquid air trap, and was found to be quite free of impurities. The viscosity as determined on the constant deflection apparatus by M. N. States[8] agreed very well with values for oxygen previously obtained. The only special precaution necessary with this method was the insertion of glass wool between the generating flask and other apparatus in order to prevent the diffusion of the manganese dioxide formed by the reaction. By using pressures above 20 to 40 cm, it was possible to liquify the oxygen in the liquid air traps, and to store it for any desired length of time. The spectrum under disruptive discharge showed no evidence of nitrogen and very little of hydrogen.

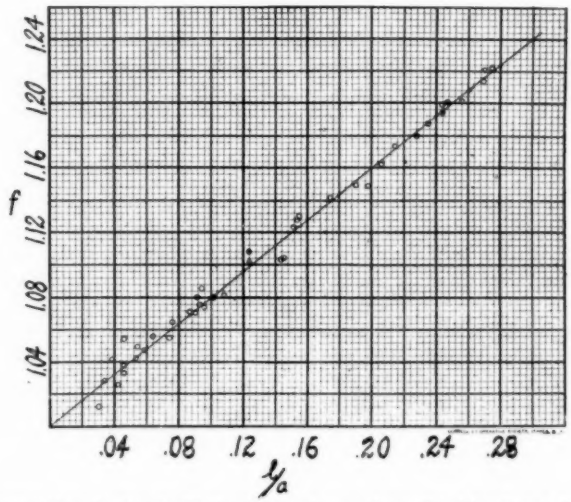

Fig. 2. Correction factor to Stokes' Law for carbon dioxide; f as a function of l/a.

The helium initially contained considerable nitrogen and some neon as well as organic vapors, etc. Everything except some of the neon and an extremely small amount of nitrogen was taken out by passing and repassing through charcoal cooled in liquid air and copper oxide heated by an electric furnace. The purification was undertaken jointly with M. N. States, who determined the viscosity and slip on the constant deflection apparatus.

Production of drops. For the work at low pressures the atomizer was of a different form from that previously used and was placed in a different position. In the earlier type (Fig. 3), the oil was allowed to run down through the lower capillary whence it was sprayed out by a stream

[8] States, Phys. Rev. **21**, 662, 1923.

of gas, the heavier drops flowing down into the bulb below while the others passed through the large tube horizontally and some were carried through the holes with the current of gas. For low pressures it was necessary to get two or three cm of oil into the upper capillary and blow it all out with high pressure. It was possible to get drops only on very rare occasions, and ordinarily so much oil came over then that after a few such successes it was necessary to take the apparatus apart and clean out the holes in the condenser.

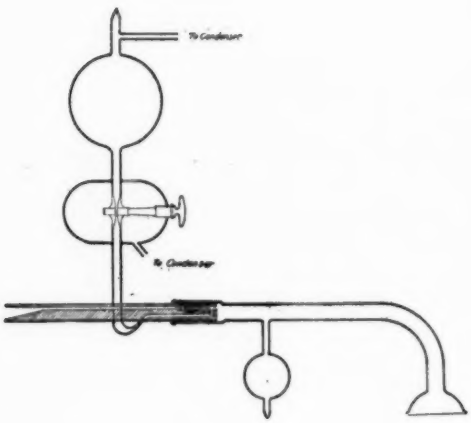

Fig. 3. First type of aspirator.

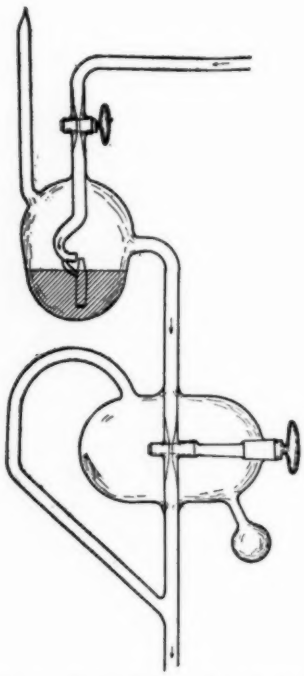

Fig. 4. Second type of aspirator.

The new arrangement (Fig. 4) is more nearly a true atomizer. It consists of a bulb with side tube for putting in oil, and one through which the gas causing the aspiration enters; attached to the latter is a small tube extending down into the oil, up which the oil is drawn by the aspirating effect of the stream of gas from the other tube. Some of the resulting fine spray passes into the side tube with the current of gas, and a few of the droplets may fall through the holes in the condenser plates directly below or be carried through by the stream of gas. Much less oil is used than in the other method and most of that is saved. Also the holes in the condenser plates did not clog up from the time the atomizer

was put on until the end of the observations. What is more important, the percentage of successful aspirations was very greatly increased. In general, larger drops were obtained when the aspirating pressure was higher. The aspirating effect was much less in both hydrogen and helium. In hydrogen, it was not possible to get drops at low pressures even with this aspirator. For helium it was discovered that increasing the aspirating pressure was sufficient to cause drops to be blown over.

Pressures up to 4.5 cm were read on a McLeod gauge. Higher pressures were read on a closed tube mercury manometer. Voltages were either read as in the viscosity work, or another electrostatic voltmeter of range 0 to 150 volts was used, or a potentiometer method was applied directly to the standard voltmeter.

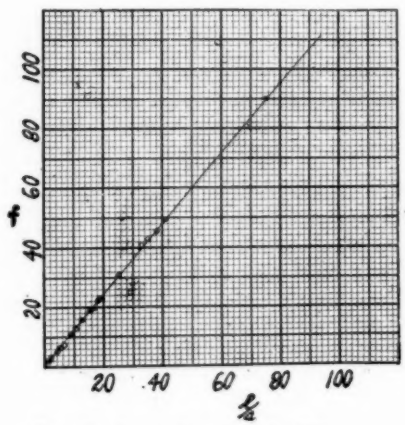

Fig. 5. Law of motion in CO_2.

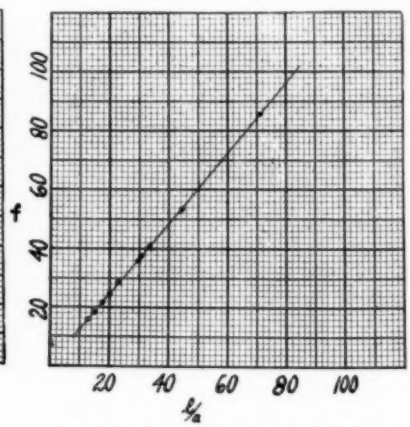

Fig. 6. Law of motion in helium.

Temperature corrections were made by Sutherland's formula as for carbon dioxide; the constant C was taken as 127 for oxygen and 80 for helium. The transformation from $1/pa$ to l/a was made in the same way as for carbon dioxide. The viscosities used were: oxygen, 2.037×10^{-4}; helium 1.962×10^{-4}. The density of the oil was determined to be 0.9153.

Experimental Results

The results of the observations are shown graphically in Figs. 5, 6, 7, and 8, and Table II contains some of the data. The variations in magnitude of the quantities measured are much greater in this investigation than in the preceding one on viscosity and slip. The potential differences between the plates was as high as 2414 volts for one drop and as low as 26.85 volts for another; the velocity of fall v_1 ranged from 0.0048 to 0.2456 cm per second, and $(v_1+v_2)_0$ from 0.001998 to 0.1941; the

number of charges on the drops was generally low (1 to 10) but values up to 60 were recorded; the radii of the drops varied between 2.614 and 13.82×10^{-5} cm; pressures ranged from 0.19 to 11 cm of mercury.

Owing to the very large scale required for the drops with large l/a, some of the points at the lower end of the range would be crowded so closely together that they cannot be shown on the curves. These points

TABLE II

Law of motion at low pressures, in carbon dioxide, oxygen and helium

Gas	v_1	$(v_1+v_2)_0$	n	a	p	l/a	f	A'
CO_2	.0312	.00885	5	13.42	10.77	.336	1.288	.882
	.0187	.01580	2– 7	9.964	10.17	.466	1.392	.842
	.0366	.00200	33–60	11.78	2.82	1.047	1.956	.913
	.0454	.01228	6–12	7.900	1.464	4.071	5.386	1.077
	.0426	.01653	4–14	7.026	1.362	4.922	6.395	1.096
	.0684	.03585	2– 4	6.359	.73	10.14	12.54	1.138
	.0944	.01151	14–17	7.115	.580	11.39	13.79	1.123
	.0324	.02186	2– 4	3.578	.835	15.88″	18.87	1.125
	.0345	.02010	3– 4	3.368	.754	18.44	22.53	1.167
	.0439	.03078	3– 4	2.843	.492	33.84	40.51	1.167
	.0579	.03178	7	3.005	.439	35.72	42.56	1.163
	.1299	.08239	3– 5	3.266	.190	75.77	89.90	1.173
Oxygen	.0314	.00524	6–18	13.82	7.168	.772	1.68	.878
	.0380	.00380	11–14	12.14	3.757	1.683	2.64	.973
	.0144	.02413	1– 4	6.34	4.599	2.623	3.58	.983
	.1985	.01804	1– 7	5.21	1.480	5.935	7.47	1.091
	.0422	.01605	4–11	3.85	.823	24.24	29.13	1.160
	.0716	.01294	7–23	3.48	.427	51.56	60.34	1.151
	.0742	.1941	5–11	3.08	.370	67.03	79.89	1.177
	.1120	.04183	7– 9	2.73	.215	129.9	152.5	1.167
Helium	.1064	.00778	16–26	8.35	1.982	12.55	15.01	1.116
	.1361	.01462	18	7.45	1.391	20.15	24.20	1.151
	.1349	.02887	6– 9	5.93	1.122	31.31	37.75	1.174
	.2456	.0166	20	7.01	1.663	44.84	53.21	1.164

are in the region where $A'=A+Be^{-Ca/l}$ is changing rapidly and are interesting on that account, but the curvature would not show on the scale to which the figures are drawn. Twenty of the thirty-six drops in carbon dioxide are plotted, while sixteen out of twenty-four points on the oxygen curve are shown. In the tables only some representative drops are given, about one-third of those observed.

In Fig. 8, the points for all the gases are plotted to the same scale, and it is quite evident that within the limits of experimental error, the constant $(A+B)$ giving the slope of the straight line asymptotic to the curve is very nearly the same for all gases. This seems to mean that at low pressures and with long mean free paths, the type of molecule has

little to do with the type of impact. It would be interesting to try materials other than oil, i.e., different types of surfaces. The slope of the average asymptotic line obtained above is about 1.175.

The empirical formula presumably breaks down when the pressure is reduced and l/a increased so that the limiting velocity becomes very great. In a perfect vacuum, of course, the limiting velocity would be infinite, and the particle under the force of gravity would be a freely

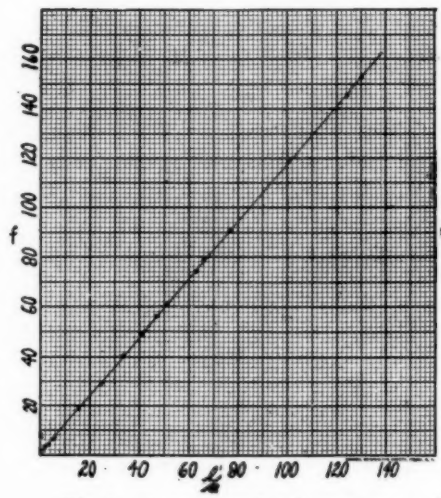

Fig. 7. Law of motion in oxygen.

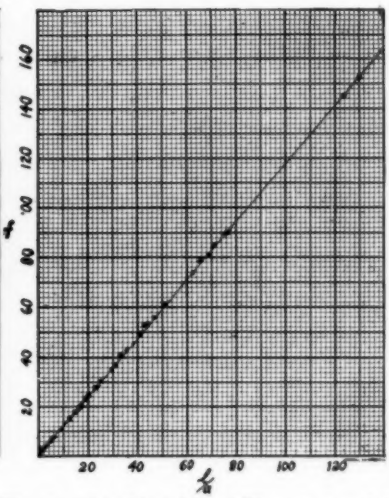

Fig. 8. Combination of Figs. 5, 6 and 7.

falling body. It is interesting to calculate the duration of the interval before it reaches approximately its limiting velocity in the actual case of the drops used.

$$dv/dt = g - 6\pi\eta av/mf$$
$$v = (mfg/6\pi\eta a)(1 - e^{-6\pi\eta at/mf})$$

Hence the limiting velocity is $mfg/6\pi\eta a$. For the drop to reach 0.99 of this, $\log_e .01 = -6\pi\eta at/mf$. If we put $f = (A+B)l/a$, then for $l/a = 100$, and $a = 3\times10^{-5}$, $t = .001$ sec. The value of the limiting velocity in this case would have been 2 mm per second.

For l/a large, the correction factor as a whole is of such importance that the law of resistance is really entirely changed, and becomes

$$(A+B)\ (l/a)\ \ F = 6\pi\eta av, \text{ or } F = 6\pi\eta a^2 v/\ (A+B)l$$

i.e., the resistance is no longer proportional to the radius of the drop, but to the cross-section.

It seems natural to compare this with the formulas deduced for the mobility of large ions. The ratio of the mass of the molecule to that of the ion may be treated as negligible. When this is done, it is found that

both Langevin's[9] and Lenard's[10] mobility formulas can be reduced to exactly the same form as the above empirical equation, but Wellisch's[11] can not. In fact, Lenard has already done this for his formula, for the ordinary slip equation, which does not apply. Wellisch's expression gives instead a result of the wrong order of magnitude, differing from the correct law by a factor depending on the ratio of the size of the molecule to that of the ion, and this shows that it cannot apply to the case in hand, where the ratio, being extremely small, is so widely different from unity. Indeed, if we follow back the derivation of this formula, we find that it is obtained from Langevin's early form, $v_0 = el/mc$, which cannot apply unless the factor referred to is unity. The correction factor which Wellisch introduced to take care of the additional resistance due to the charge on the ion reduces to unity for oil drops of the sizes used, and this might be regarded as explaining the observed fact that the mobilities of the oil drops under purely mechanical forces are entirely independent of their electrical charges. Whatever the interpretation of the constant $(A+B)$ in the empirical equation may be, it is certainly surprising that the form of the law deduced by Langevin and Lenard for the case of ionic carriers should hold with absolute accuracy for the observable spheres, many times the size of the largest ions.

The author wishes to acknowledge his indebtedness to Dr. W. Stenstrom, with whom the author did the earlier part of the work on carbon dioxide at low pressures; also to A. C. Findley, W. V. Houston, R. E. Harris, and K. S. Woodcock, for assistance at various times during the progress of the observations. Especially does the author desire to thank those under whose direction the work was carried out, Professor R. A. Millikan (who suggested the problem) and Professor H. G. Gale.

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March 15, 1923.[12]

[9] Langevin, Ann. de Chem. et de Phys. **5**, 245, 1905.
[10] Lenard, Ann. der Phys. **61**, 665, 1920.
[11] Wellisch, Phil. Trans. Roy. Soc. **209**, 272, 1909.
[12] This paper was originally submitted in November, 1922.

THERMAL CONDUCTIVITIES OF SOME METALS IN THE SOLID AND LIQUID STATES

By W. Byron Brown

Abstract

Thermal conductivities of some metals and eutectic alloys above and below their melting points, 50° to about 400° C.—*A guard ring method of measurement* was used. A cylindrical rod of the metal, 1.5 cm in diameter and 12 cm long was surrounded by a slate tube and outside that a hollow brass cylinder. Both rod and cylinder were independently heated electrically at the top and cooled by flowing water at the bottom so as to maintain the same temperature gradient in both, as shown by thermocouples. The input of energy into the rod was corrected slightly for heat leakage and divided by the temperature gradient times the area to get the conductivity. *The conductivities of tin and cadmium* decrease at the melting point by over 1/3 and ½ respectively. *For thallium*, there is a drop of 1/10 at about 120° C. The temperature coefficients are about the same before and after melting, being -5×10^{-5} (Sn), $+21\times10^{-5}$ (Cd), $+8\times10^{-5}$ (Th). *For the eutectics: Sn .92, Zn .08; Sn .62, Pb .38; Pb .87, Sb .13; Pb .46, Bi .54;* the temperature coefficients for the liquids are all positive constants and have values at 300° C—from .0011 (Pb−Bi) to .0030 (Pb−Sb)—close to those found for gases at that temperature, indicating that the mechanism is similar in the two cases. Below the melting point the curves vary, one increasing with temperature (Sn−Zn), two decreasing, and one reaching a maximum (Pb−Sb). The sudden decrease on melting varies from 2/3 for (Sn−Zn) and (Pb−Sn) to 1/10 for (Bi−Pb).

Polymorphic change in thallium at 120° C is indicated by the conductivity results.

NORTHRUP and Pratt[1] and A. W. Porter and F. Simeon[2] have studied the change in the thermal conductivity of tin, bismuth, sodium and mercury on fusion. Konno[3] has measured the change in the conductivity of tin, lead, bismuth, zinc, aluminum and antimony from room temperature to about 700°C. Hornbeck[4] measured the conductivity of a sodium-potassium alloy in both the liquid and the solid state. No other work appears to have been done on the change of the thermal conductivity of metals and alloys at fusion and on the variation with temperature of the thermal conductivity of the molten metals. In view of the limited amount of data available it appeared worth while to extend these observations to other metals and alloys.

[1] Northrup and Pratt, Jour. Franklin Institute, **184**, 675, 1917
[2] Porter and Simeon, Proc. Phys. Soc. **27**, 307, 1915
[3] Konno, Science Reports, Tohoku Imperial Univ. (1) **8**, 177, 1919
[4] Hornbeck, Phys. Rev. (2) **2**, 217, 1913.

Method of Measurement

The specimen to be measured (Fig. 1) was in the form of a cylindrical rod *R*, 1.5 cm in diameter and 12 cm long, encased in a slate tube *S*. Heat was supplied at the top by a heating coil of nichrome wire wound on a copper core *C*, power being furnished by a storage battery. The voltage across it was kept constant to 1/5000 by means of a potentiometer arrangement which balanced a definite fraction of the voltage against an Edison storage cell in series with a galvanometer. It was found that

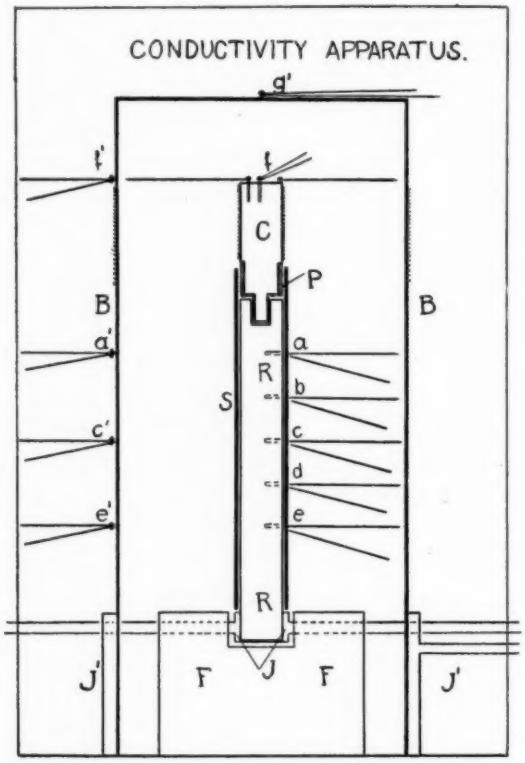

Fig. 1

molten metals dissolved the copper quite rapidly, forming an alloy with a quite different conductivity. To prevent this action a steel shell *P* about 2 mm thick was screwed tightly over the lower part of the copper core. This was then screwed into the top of the specimen. The heating coil was covered with a thick layer of cement (a mixture of 1 part sodium silicate to 1 part powdered feldspar) to prevent oxidation. The rod *R* was cooled at the bottom by cold water circulating through a small jacket *J*. The flow was kept constant by an overflow tank which main-

tained a constant head. Outside the slate tube S was a brass tube B, 10 cm in diameter, heated at the top by a coil of wire and cooled at the bottom by a water jacket J' similar to J. By controlling the current supplied to the shield heater, the same temperature gradient could be established in the specimen and in the jacket. A second brass tube, 17.2 cm in diameter, surrounded the shield described above, and the annular spaces between the two shields and the slate tube were filled with very finely powdered, calcined magnesia.

The temperature gradient in the rod was measured by means of five thermo-couples, a, b, c, d, e, 1.5 cm apart. To ensure accurate spacing of the junctions, they were hard-soldered into tapered steel bushings about 1.5 mm in diameter at the large end and 5 mm long and then calibrated by means of a travelling microscope. The holes in the rod were reamed out until these bushings fitted into them flush with the surface. The wires were sealed into the slate by the cement described above. The cold junctions were in an insulated oil bath at room temperature, the temperature being estimated to 0°.01 C on a mercury thermometer.

Thermo-junctions were placed on the brass tube B at the points a', c', e', f', and g', directly opposite the corresponding junctions in the rod. The junctions were held in contact with the tube by means of suitable screws, and the lead wires were insulated by lavite bushings.

The thermal electromotive forces were measured by means of a slide-wire potentiometer with necessary extension coils. It was calibrated by means of a Leeds and Northrup high precision Wheatstone bridge, which was used to compare each hundreth part of the slide wire with the total and each resistance coil with the slide wire and with the total potentiometer resistance. The table of corrections thus found was used in all subsequent work. The largest correction was 0°.14 C, most of them being of the order of 0°.04 C.

The thermo-couples were calibrated at the following points[5] (the other junction being in the oil bath as usual).

	Temp.	Pressure coefficient (deg./cm Hg).
1. Ice (m. p.)	0°.00	
2. Water (b. p.)	100°.00	0.368
3. Aniline (b. p.)	183°.9	0.51
4. Diphenylamine (b. p.)	302°	0.66*
5. Sulphur (b. p.)	444°.7	0.91

* Estimated from values for similar substances.

It was found possible to represent these points quite accurately by means of two parabolic equations, one covering the range 0°-184° and the other

[5] These values were taken from "Recueil de Constantes Physiques" Societe Francaise de Physique, 1913.

the range 184°-450°. A table was constructed by means of these equations and used to find the approximate temperature. Each couple was calibrated separately and its deviations from the above table tabulated, thus enabling the true temperature to be found.

Theory of the Measurements

The conductivity was calculated from the usual equation,

$$H = KAt(d\theta/dx) \tag{1}$$

If W = watts flowing and J = mechanical equivalent of heat, then the equation for the thermal conductivity K may be written,

$$K = W/JA(d\theta/dx) \tag{2}$$

If it is desired to apply (2) to a particular point such as b or c, then it is necessary to know the heat which is actually flowing down the rod at that point. This is found by subtracting from the power input, the heat leakage to or from the coil and rod above the point under consideration. For convenience the heat leakage, Δw, is divided into three parts.

The first part Δw_1 is the heat lost from the top and sides of the heating coil C and the case S above the point b by transfer through the magnesia and conduction along the lead wires. It is calculated by the equation,

$$\Delta w_1 = M\Delta\theta' \tag{3}$$

where $\Delta\theta'$ is the approximate temperature difference between the rod and enclosure, and M is a constant found by experiment. Δw_1 usually amounts to from 4 to 7 per cent of W.

The second part Δw_2 is the heat lost from the sides between b and the point where K is being determined. It is given by

$$\Delta w_2 = N\Delta\theta_m\Delta x \tag{4}$$

where N = constant found by experiment,

$\Delta\theta_m$ = mean temperature difference between rod and enclosure,

Δx = distance from b to the point considered.

This correction is negligible in the solid state and less than 1.5 per cent in the liquid state.

The third part Δw_3 is the heat conducted by the slate case S. It is given by

$$\Delta w_3 = CJk'A'(d\theta/dx) \tag{5}$$

where C = constant found by experiment;

k' = conductivity of the slate;

A' = area of slate.

This correction is usually about 6 per cent of w.

These corrections sometimes have different signs so that their sum Δw varies from 2 to 8 per cent of w. The error in Δw does not exceed 10 per cent, so that the effect on W is about 1 per cent or less.

In equation (2), therefore, W is given by

$$W = IV - \Delta W \tag{6}$$

where I = current in amperes and V = voltage drop over heating coil.

Both A and Δx change with the temperature on account of the expansion of the metal and case. Putting $A = A_0(1+\lambda t)$, Eq. (2) becomes

$$K = W/JA_0(1+\lambda t)\ (d\theta/dx) \tag{7}$$

Two slightly different modes of treatment were used in finding $d\theta/dx$, one when the metal was solid throughout and the other when it was partially liquid. In the latter case, the temperature difference between two adjacent junctions was divided by the distance between them and the quotient used as the value of $d\theta/dx$ midway between these junctions. In the former case, the temperature differences between adjacent junctions were much smaller and consequently the change in K between them much less. Hence the difference between every other junction was divided by the corresponding distance. This gave three values for $d\theta/dx$ at temperatures rather near together. The average of the three was used to find $d\theta/dx$ at the middle junction c.

Observations and Results

An estimate was made of the power needed to produce equilibrium for a desired region of temperature. This was then supplied and the apparatus allowed to heat until steady temperatures were attained. The couples at a and a' were connected in opposition through a fairly sensitive galvanometer and the power supplied to the enclosure B adjusted until the galvanometer showed no deflection or a very small one. From two to four hours were required according to the nature of the material under test. Readings of current, voltage and e.m.f. of the thermocouples were taken both direct and reversed, and with the exception of the couples on B, needed only for the calculation of correction terms, were repeated in inverse order. All readings were then reduced to the mean time of the observations, though the drift was never large.

The results are given in Tables I and II and also plotted in Figs. 2 and 3.

Discussion of Results

The values given in the table for cadmium were obtained by heating the specimen continuously from one temperature to the next higher. Lower values of K, increasing slowly with time, were obtained when the specimen was heated rapidly to a high temperature. For example, measurements on a specimen of cadmium heated to 262°C after cooling overnight gave the value of 0.197. After 3 hours at approximately this

temperature the conductivity had increased to 0.204 at 230°C. Cohen[6] has reported three allotropic modifications of cadmium, the transition points being 65° and 95°C. If the form stable at the higher temperature

TABLE I.

Conductivity of pure metals

tin (m. p. 232° C)		cadmium (m. p. 320° C)		thallium (m. p. 302° C)	
Temp.	Cond.	Temp.	Cond.	Temp.	Cond.
50	.1428	45	.200	45	.0934
102	.1404	99	.209	72	.0938
147	.1390	125	.213	88	.0957
160	.1368	165	.221	90	.0958
209	.1297	221	.237	113	.0976
m. p.	.....				
264	*.0815	240	.239	125	.0919
		m. p.	....	149	.0927
291	.0752	355	.106	217	*.111
347	.0767	358	.105	m. p.	.....
		380	.105	353	*.059
		435	.119		

* Doubtful

TABLE II.

Conductivity of eutectic alloys

tin : .92 zinc : .08 (m. p. 200° C)		tin : .62 lead : .38 (m. p. 180° C)		lead : .87 antimony : .13 (m. p. 248° C)		lead : .46 bismuth : .54 (m. p. 130° C)	
Temp.	Cond.	Temp.	Cond.	Temp.	Cond.	Temp.	Cond.
35	.1425	40	.1178	34	.0630	42	.0236
64	.1469	70	.1177	43	.0637	60	.0229
91	.1474	102	.1125	51	.0644	92	.0230
115	.1497	122	.1120	76	.0661	m. p.	.....
120	.1440	124	.1119	97	.0670	166	.0226
148	.1505	125	.1150	118	.0678	185	.0229
m. p.	.....	139	.1115	120	.0665	200	.0233
215	.057	m. p.	.....	155	.0664	236	.0244
343	.0731	236	.0553	168	.0666	285	.0258
433	.0878	239	.0533	190	.0650		
		310	.0610	m. p.	.....		
		336	.0615	316	.0386		
		420	.0710	325	.0396		
				372	.0455		
				382	.0456		
$dK/Kd\theta = .0020$*		$dK/Kd\theta = .0014$*		$dK/Kd\theta = .0030$*		$dK/Kd\theta = .0011$*	

* Temperature coefficient $dK/Kd\theta$ at 300° C.

[6] Cohen, Kon Acad. van Wet. te Amsterdam **16**, 489 and **17**, 1050

has a higher conductivity than the other forms, the positive temperature coefficient can be explained by the transition even though the conductivity of one form decreases slightly with rising temperature.

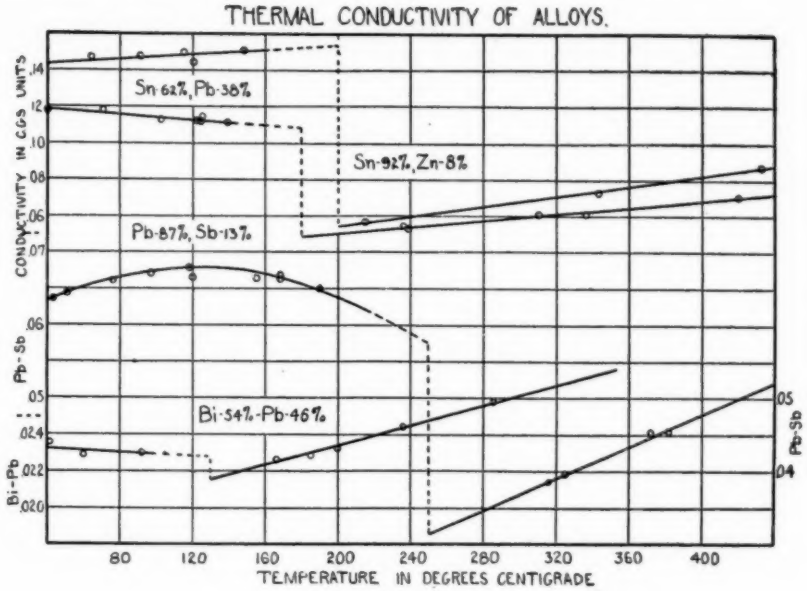

Fig. 2

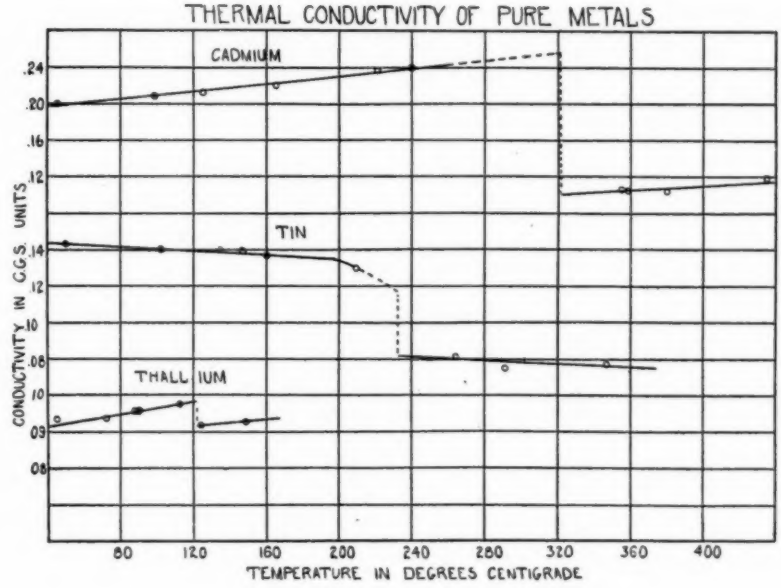

Fig. 3

A similar erratic behavior was observed in the case of thallium and consequently it, as well as the alloys, were heated continuously from one temperature to the next without shutting off the power over night. The last two observations were not plotted because the specimen burned out at the top before the set was quite finished and no more thallium was available. They are included in the table because they show, qualitatively at least, the change in the conductivity of thallium on fusion.

No previous data were available for comparison above 100°C except in the case of tin. At 100°C, however, the following were found

TABLE III

Conductivity of tin and cadmium at 100° C

Lorenz[7]:	.1432 (Sn)	.204 (Cd)
J and D[8]:	.1358 (Sn)	.216 (Cd)
Lees[9]:	.147* (Sn)	.210* (Cd)
Mean (other observers):	.1420 (Sn)	.210 (Cd)
Brown;	.1405 (Sn)	.209 (Cd)

* Extrapolated from 18° C by means of J. and D.'s temperature coefficient.

Konno,[3] using a relative method, found the ratio of the thermal conductivity of molten tin at 292°C to solid tin at 209°C to be .081/.143 = .57. The value found here is .0752/.1297 = .579.

Northrup and Pratt's[1] observations give a rough value of 0.32 for this ratio. This low value can be explained by the fact that the heat loss in their experiments with molten tin was relatively larger than that with solid tin, both on account of the higher temperature and the lower conductivity of molten tin. Since in both cases the heat loss from their apparatus was very large, the difference in the two cases might become excessive.

All the alloys tested show a rather rapid increase of thermal conductivity with increasing temperatures. This agrees with the observations of Hornbeck,[4] who found the same for the Na-K alloy he tested.

The Kinetic Theory of gases shows that K for gases is proportional to η the viscosity, and that η is proportional to T^n where T is the absolute temperature and n is a constant depending on the nature of the gas.[10] Therefore $K = CT^n$ and

$$\frac{1}{K} \cdot \frac{dK}{dT} = \frac{n}{T} \tag{8}$$

When $T = 573°$ K, the values of n/T range from .0012 for H to .0017 for CO_2 while the coefficients of our molten alloys go from .0011 to .0030.

[7] Lorenz, Wied, Ann. **13**, 422, 1881

[8] Jaeger and Diesselhorst, Abh. d. Phys.—Techn. Teichsanstalt, **3**, 269, 1900

[9] Lees, Phil. Trans. **208**, 381, 1908

[10] Jeans, Dynamical Theory of Gases, 2nd. Ed. p. 302

It appears probable, therefore, that the mechanism of heat conduction in these alloys is quite similar to that which exists in the case of gases.

In conclusion, I wish to acknowledge the constant encouragement and help of Professor Alpheus W. Smith, who suggested the subject and supervised the work throughout, and express my thanks to Drs. F. B. Silsbee and M. S. Van Dusen of the Bureau of Standards, who read the manuscript.

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MAGNETIC AND NATURAL ROTATORY DISPERSION IN ABSORBING MEDIA

By E. O. Hulburt

Abstract

Electron Theory of Magnetic and Natural Rotatory Dispersion in Absorbing Media.—On the basis of the electron theory of Lorentz, theoretical formulas have previously been derived for rotatory dispersion in perfectly transparent liquids, but on comparison with experimental results, a discrepancy was found which seemed to be due to the absorption. In the present paper, the theory has been extended to take account of absorption, and by making certain approximations, simplified formulas are obtained which give the rotation for wave-lengths sufficiently removed from the critical wave-length, provided the refractive index and extinction coefficient conform to the Lorentz dispersion equations with one resonance frequency. The equation of magnetic rotation in isotropic media agrees closely with experimental results for CS_2 and α-monobrom-naphthalene. It is suggested that the theoretical equation for natural rotation: $\theta/l = r_1 + (2\pi^2\gamma_1/\lambda^2)\,[\mu_0^2 - 1/(1+\kappa_0^2)]$, (where μ_0 and κ_0 are refractive index and extinction coefficient, respectively, and r_1 and γ_1 are constants), may be assumed to describe the phenomenon in any medium, whether μ_0 and κ_0 satisfy the Lorentz dispersion equations or not, but this has not yet been tested experimentally.

Introduction

IN TWO recent communications[1] formulas for the natural and magnetic rotatory dispersion in transparent liquids were developed from the electron theory of H. A. Lorentz and were submitted to experimental test by means of data obtained for the purpose. It was found that the values of the magnetic rotation angles calculated from the theoretical formulas increased with decrease of wave-length more rapidly than the observed angles and it was pointed out that the discrepancy might be attributed, in part at least, to the neglect in the theory of the effect of absorption. In the present paper absorption of the radiation in the medium has been considered from a theoretical standpoint and more complete rotatory dispersion formulas have been derived.

The theory of magnetic rotatory dispersion, i.e., the Faraday effect, and of natural rotatory dispersion, i.e., the Biot effect, has been excellently stated by Drude[2] and Voigt.[3] H. A. Lorentz[4] has further con-

[1] Hulburt, Astrophysical Journal, 54, 45 and 116, 1921.
[2] Drude, Lehrbuch der Optik, 1906.
[3] Voigt, Magneto- und Electrooptik, 1908.
[4] H. A. Lorentz, Theory of Electrons 1916, p. 132.

tributed to the electron theory of the Faraday phenomenon, obtaining formulas similar to those of Drude and of Voigt but with a different interpretation of the constants of the equations. The formulas when reduced by simplifying assumptions were found to be in accord with the observed magnetic rotation in the case of the sodium flame and other experiments.[5] It seems, however, that the general formulas have not been sufficiently developed to be useful for the consideration of absorbing media.

Magnetic Rotatory Dispersion

We use the electron theory of dispersion as given by H. A. Lorentz and restrict the discussion to isotropic media in which the temperature remains constant. Let ξ and E_x be the X-components of the displacement of the electron from its equilibrium position and the electric force, respectively, and η, ζ, E_y, and E_z be the Y and Z components of the quantities. The components of the "restoring force" and of the "frictional force" with which the medium acts upon the electron are $f\xi$, $f\eta$, $f\zeta$ and $\beta\dot{\xi}$, $\beta\dot{\eta}$, $\beta\dot{\zeta}$, respectively, where f and β are positive constants. The charge on the electron is denoted by e, its mass by m; N is the number of such electrons per unit volume. σ is a constant which Lorentz has shown to be approximately one-third for isotropic media. We shall denote the external magnetic field by H and shall suppose it to have the direction of the axis of Z, which is also the direction of the propagation of the light. The magnetic permeability of the medium is taken to be unity. All quantities are expressed in c.g.s. e.m. units. In Newtonian notation the equations of motion of the dispersion electrons of a single type are, then,

$$\left.\begin{aligned} m\ddot{\xi} &= e(E_x+4\pi c^2\sigma Ne\xi)-f\xi-\beta\dot{\xi}+He\eta, \\ m\ddot{\eta} &= e(E_y+4\pi c^2\sigma Ne\eta)-f\eta-\beta\dot{\eta}-He\dot{\xi}, \\ m\ddot{\zeta} &= e(E_z+4\pi c^2\sigma Ne\zeta)-f\zeta-\beta\dot{\zeta} \end{aligned}\right\} \qquad (1)$$

Let e be the base of natural logarithms, and let all dependent variables of (1) contain the time only in the factor $e^{i2\pi\kappa/\lambda}$, where c/λ is the frequency, λ the wave-length of the vibration in vacuum, c is the velocity of light in vacuum, and i is $\sqrt{-1}$. The solution of (1) yields two vibrations, circularly polarized in opposite directions, whose refractive indices μ_1 and μ_2 and extinction coefficients κ_1 and κ_2 are given by the relations

$$\frac{1}{\sigma+\dfrac{1}{[\mu(1-i\kappa)]^2-1}}=\frac{C_s}{1/\lambda^2{}_s-1/\lambda^2+ib_s/\lambda\pm Hhs/\lambda}, \qquad (2)$$

where $C_s=N_se^2/\pi m_s$, $b_s=\beta_s/2\pi cm_s$, $h_s=e/2\pi cm_s$.

[5] Lorentz, loc. cit., p. 164.

The details of this solution are here omitted for they are essentially the same as those given by Lorentz. The subscript s is used to denote the s'th type of electron. c/λ_s is the frequency of the natural undamped vibration of the electron, and is equal to $1/2\pi\sqrt{f_s/m_s}$. When the plus sign is used in the right hand term of (2), μ is μ_1 and κ is κ_1. When the minus sign is used μ is μ_2 and κ is κ_2. We see that under the influence of the magnetic field the medium is doubly refracting and possesses two different degrees of transparency.

The *absorption coefficient* K of the nonmagnetized medium is defined by the relation

$$K=(1/2l)\ \log_e I_0/I, \tag{3}$$

where I_0 is the intensity of the incident radiation and I is the intensity, after passing through a layer of the medium of thickness l. In obtaining (2) from (1) we have made the substitution

$$\kappa=\lambda K/2\pi\mu. \tag{4}$$

From (3) and (4) the extinction coefficient κ is expressed by

$$\kappa=(\lambda/4\pi\mu l)\ \log_e I_0/I. \tag{5}$$

By means of (5), κ may be determined from measurements of the transmitted radiation.

Eq. (2) describes the refractive indices and extinction coefficients in terms of the constants of a single type of dispersion electron. There may be other types of dispersion electrons in the medium with constants peculiar to the type, so that in the more general case the right hand member of (2) may be assumed to be a summation of similar terms, one term for each type. For this case the complete dispersion formula is

$$\frac{1}{\sigma+\dfrac{1}{[\mu(1-i\kappa)]^2-1}}=\sum\frac{C_s}{1/\lambda_s^2-1/\lambda^2+ib_s/\lambda\pm Hh_s/\lambda}. \tag{6}$$

We assume we are dealing with a region of the spectrum in which the change of the refractive index with wave-length is determined by the electrons of a single type, denoted by the subscript 1, so that in the summation of (6) all the terms except one may be replaced by a quantity q_1, which is independent of λ and H. Then (6) becomes

$$\frac{1}{\sigma+\dfrac{1}{[\mu(1-i\kappa)]^2-1}}=q_1+\frac{C_1}{1/\lambda_1^2-1/\lambda^2+i\ b_1/\lambda\pm Hh_1/\lambda}. \tag{7}$$

Separating the real and imaginary parts of (7) by a transformation similar to one used by Havelock,[6] gives

[6] Havelock, Proc. Roy. Soc., **86**, 1, 1912.

$$\mu^2(1-\kappa^2)/q_1' = 1+g\lambda^2(\lambda^2-\lambda_2'^2)/[(\lambda^2-\lambda_2'^2)^2+g'^2\lambda^2],$$
$$2\mu^2\kappa/q_1' = gg'\lambda^3/[(\lambda^2-\lambda_2'^2)^2+g'^2\lambda^2], \quad (8)$$

where q_1', λ_2', g and g' are defined by the following equations;

$$q_1' = [1+q_1(1-\sigma)]/(1-q_1\sigma), \quad \lambda_2'^2 = \lambda_1'^2(1\mp Hh_1\lambda),$$
$$1/\lambda_1'^2 = 1/\lambda_1^2 - C_1\sigma/(1-q_1\sigma), \quad g = C_1\lambda_1'^2/(1-q_1\sigma)^2q_1', \; g' = b_1\lambda_1'^2. \quad (9)$$

Again, just as in the case of Eq. (2), Eqs. (8) are each two formulas, giving μ_1 and κ_1 when the minus sign is used in the expression for λ_2' in (9), and μ_2 and κ_2 when the plus sign is used. It will abbreviate our expressions to replace the right hand terms of (8) by A_1, A_2, B_1 and B_2, obtaining

$$\mu_1^2(1-\kappa_1^2)/q_1' = A_1, \quad \mu_2^2(1-\kappa_2^2)/q_1' = A_2,$$
$$2\mu_1^2\kappa_1/q_1' = B_1, \quad 2\mu_2^2\kappa^2/q_1' = B_2. \quad (10)$$

We shall be concerned with the dispersion formulas for the nonmagnetized medium. These are obtained by placing $H=0$ in Eqs. (8), which leads to

$$\mu^2(1-\kappa^2)/q_1' = 1+g\lambda^2(\lambda^2-\lambda_1'^2)/[(\lambda^2-\lambda_1'^2)^2+g'^2\lambda^2],$$
$$2\mu^2\kappa/q_1' = gg'\lambda^3/[(\lambda^2-\lambda_1'^2)^2+g'^2\lambda^2], \quad (11)$$

where q_1', λ_1', g and g' are defined by (9) and μ and κ, now physically single valued, refer to the nonmagnetized medium.

Let θ be the angle in radians of the rotation of the plane of polarization produced by a thickness l of the magnetized, doubly refracting, medium. It may be shown[7] that

$$\theta = (\pi l/\lambda)\,(\mu_2-\mu_1). \quad (12)$$

Solving (10) for μ_1 and μ_2 and substituting these values in (12) gives

$$\theta = (\pi l/\lambda)\sqrt{q_1'/2}\left\{\sqrt{A_2+\sqrt{A_2^2+B_2^2}}-\sqrt{A_1+\sqrt{A_1^2+B_1^2}}\right\} \quad (13)$$

This expression is rather cumbersome, so we change it into a more convenient form by availing ourselves of the fact that in most instances $Hh_1\lambda$ is small compared to unity. When the terms containing the square and higher powers of $Hh_1\lambda$ are neglected, (13) becomes

$$\theta = \pi lHh_1\lambda_1'^2\left\{[q_1'g\lambda^2/\mu(1+\kappa^2)]\;[(\lambda^2-\lambda_1'^2)^2-g'^2\lambda^2]/[(\lambda^2-\lambda_1'^2)^2+g'^2\lambda^2]^2\right.$$
$$\left.+[8\mu^3\kappa^3/(1+\kappa^2)q_1']\;[(\lambda^2-\lambda_1'^2)/gg'\lambda^3]\right\}. \quad (14)$$

We may obtain a less expansive value for θ by assuming that the changes in κ occasioned by the magnetic field produce negligibly small changes in θ, or in other words, by assuming that $\kappa=\kappa_1=\kappa_2$. Making use of this assumption as well as of the smallness of $Hh_1\lambda$ the approximate values of μ_1 and μ_2 were obtained from the two Eqs. (10) and were introduced into (12). This gave

$$\theta = [\pi lHh,\; q_1'\;g\lambda^2\lambda_1'^2/\mu(1-\kappa^2)]\;[(\lambda^2-\lambda_1'^2)^2-g'^2\lambda^2]/[(\lambda^2-\lambda_1'^2)^2+g'^2\lambda^2]^2 \quad (15)$$

[7] Drude, loc. cit., p. 396.

Because of the approximations, formulas (14) and (15) are in close accord with the exact formula (13) for wave-lengths sufficiently removed from the critical wave-length λ_1' but are invalid for wave lengths in the region of λ_1'. Furthermore, all the formulas are permissible only when the refractive index and the extinction coefficient of the medium conform to the dispersion equations (11).

For zero absorption (14) and (15) each reduce to

$$\theta = \pi l H h_1 [q_1' g/\mu] [\lambda_1'^2 \lambda^2/(\lambda^2 - \lambda_1'^2)^2], \tag{16}$$

and this in turn is changed by means of (9) to

$$\theta = \pi l H h_1 C_1 \{[\sigma(\mu^2 - 1) + 1]^2/\mu\} \{\lambda_1^4 \lambda^2/(\lambda^2 - \lambda_1^2)^2\}. \tag{17}$$

This is the same as formula (12) of a former paper,[8] and if σ is placed equal to zero, (17) agrees with a formula of Voigt when his quantities are expressed in c.g.s. e.m. units.

In the paper just cited the measured magnetic rotation angles of a number of liquids for wave-lengths of light in the visible region of the spectrum were found to be less than the angles calculated by means of (17) for the shorter wave-lengths. In order to apply the more complete formulas (14) or (15) the extinction coefficients must be known. These have not been measured directly for the substances concerned, but in the cases of carbon disulphide and α-monobromnaphthalene, values of g' are available which were derived from measurements of the ultraviolet reflecting powers[9] of the liquids. With these values of g', formula (15) gave close agreement with the observations throughout the visible spectrum. For illustration, the approximate calculations for carbon disulphide are given in Table I. From refractive index data in the visible spectrum, considering absorption negligible, it is found that $q_1' = 1.7544$, $g = 0.434$, and $\lambda_1' = 228.4\mu\mu$. From ultraviolet reflection data $g' = 0.5136 \times 10^{-5}$.

TABLE I

Wave-length	θ Magnetic Rotation Angles		
	from observation	from (16)	from (15)
430$\mu\mu$	22.1°	23.4°	22.0°
500	15.3	15.6	15.3
640	8.3	8.3	8.3

NATURAL ROTATORY DISPERSION

We postulate an optically active medium in which the temperature remains constant, free from the influence of an external magnetic field.

[8] Astrophysical Journal, 54, 45, 1921.
[9] Astrophysical Journal, 44, 1, 1917.

If the axis of Z be the direction of propagation of the light we find for the equations of motion of the dispersion electrons of a single type in Newtonian notation and c.g.s. e.m. units,

$$\left.\begin{aligned} m\ddot{\xi} &= e[E_x+4\pi c^2\sigma Ne\xi+\gamma\ \mathrm{curl}_x\bar{E}]-f\xi-\beta\dot{\xi}, \\ m\ddot{\eta} &= e[E_y+4\pi c^2\sigma Ne\eta+\gamma\ \mathrm{curl}_y\bar{E}]-f\eta-\beta\dot{\eta}, \\ m\ddot{\zeta} &= e[E_z+4\pi c^2\sigma Ne\zeta+\gamma\ \mathrm{curl}_z\bar{E}]-f\zeta-\beta\dot{\zeta}. \end{aligned}\right\} \tag{18}$$

All the quantities in the expressions except γ have been defined in the preceding section. γ is a constant which depends upon the anisotropy of of the medium and may be positive or negative. The explanation of the formation of these equations is given in the communication referred to in the introduction.[1]

The solution of (18) is carried out in the same way as in the case of equations (1) and is found to yield two vibrations circularly polarized in opposite directions, whose refractive indices μ_1 and μ_2 and extinction coefficients κ_1 and κ_2 are expressed by the relations

$$\frac{1}{\sigma+\dfrac{1-[2\pi\gamma/\lambda][\mu_1(1-i\kappa_1)]}{[\mu_1(1-i\kappa_1)]^2-1}}=\frac{C_s}{1/\lambda_s^2-1/\lambda^2+i\,b_s/\lambda}, \tag{19}$$

$$\frac{1}{\sigma+\dfrac{1+[2\pi\gamma/\lambda][\mu_2(1-i\kappa_2)]}{[\mu_2(1-i\kappa_2)]^2-1}}=\frac{C_s}{1/\lambda_s^2-1/\lambda^2+i\,b_s/\lambda}, \tag{20}$$

where C_s, b_s, and λ_s have the same meanings as before. Equations (19) and (20) describe the refractive indices and extinction coefficients in terms of the constants of a single type of dispersion electron. Since there may be other types of dispersion electrons in the medium, in the more general case the right hand members of (19) and (20) may be assumed to be summations of similar terms, one term for each type. However, if we deal with a region of the spectrum in which the changes of the refractive index and extinction coefficient with wave-length are determined by the electrons of a single type, denoted by the subscript 1, in the summations just mentioned all the terms except one may be replaced by a quantity q_1 which is independent of λ. Then (19) and (20) become, respectively,

$$\frac{1}{\sigma+\dfrac{1-[2\pi\gamma/\lambda][\mu_1(1-i\kappa_1)]}{[\mu_1(1-i\kappa_1)]^2-1}}=q_1+\frac{C_1}{1/\lambda_1^2-1/\lambda^2+ib_1/\lambda}, \tag{21}$$

$$\frac{1}{\sigma+\dfrac{1+[2\pi\gamma/\lambda][\mu_2(1-i\kappa_2)]}{[\mu_2(1-i\kappa_2)]^2-1}}=q_1+\frac{C_1}{1/\lambda_1^2-1/\lambda^2+i\,b_1/\lambda}. \tag{22}$$

If γ is zero in (21) or (22) we obtain quantities μ_0 and κ_0 defined by the expression

$$\frac{1}{\sigma+\dfrac{1}{[\mu_0(1-i\kappa_0)]^2-1}}=q_1+\frac{C_1}{1/\lambda_1^2-1/\lambda^2+ib_1/\lambda}. \tag{23}$$

Comparing (21), (22), and (23) we find

$$[\mu_0(1-i\kappa_0)]^2=\mu_1(1-i\kappa_1).\mu_2(1-i\kappa_2). \tag{24}$$

The real and imaginary parts of (21) and (22) may be separated, κ_1 and κ_2 may be eliminated, and μ_1 and μ_2 determined in terms of the dispersion constants. These values of μ_1 and μ_2 may be then introduced into equation (12) to determine θ. The expressions are unwieldy and in the present instance we choose to avoid such a straight-forward procedure and to simplify the equations by means of an approximation. We leave out of consideration the difference in transparency of the anistropic medium for the two kinds of circularly polarized light and assume that $\kappa_0=\kappa_1=\kappa_2$. This assumption is not permissible for wave-lengths near the critical region λ_1, but is closely valid for spectral regions removed from this. Eq. (24) then reduces to $\mu_0^2=\mu_1\mu_2$, which shows that μ_0 is the geometrical mean of μ_1 and μ_2. If the refractive index of the optically active medium be determined directly by a refractometer, the value obtained may be interpreted to be almost exactly μ_0. In like manner a measurement of the absorption coefficient by the usual transmission methods gives a number which may be taken to be K_0. The extinction coefficient κ_0 is obtained from this by means of the relation $\kappa_0=\lambda K_0/2\pi\mu_0$.

Introducing (21) and (22) into (12) and making use of the above assumption, we obtain

$$\theta=(2\pi^2\gamma l/\lambda^2)\ \{[\mu_0(1-i\kappa_0)]^2-1\}/(1-i\kappa_0,) \tag{25}$$

where θ is now a complex quantity. The real part of θ is given by

$$\theta=(2\pi^2\gamma l/\lambda^2)\ [\mu_0^2(1+\kappa_0^2)-1]/(1+\kappa_0^2). \tag{26}$$

By the same reasoning as before we note that several types of electrons may contribute to the rotation and therefore (26) may be written in the general case,

$$\theta=\Sigma(2\pi^2\gamma l/\lambda^2)\ [\mu_0^2(1+\kappa_0^2)-1]/(1+\kappa_0^2). \tag{27}$$

When κ is zero formula (27) agrees with one obtained by Drude. Again, considering that only a single type of electron is important in determining the variation of θ with λ for the region of the spectrum under investigation, (27) simplifies to

$$\theta=r_1 l+(2\pi^2\gamma_1 l/\lambda^2)\ [\mu_0^2(1+\kappa_0^2)-1]/(1+\kappa_0^2). \tag{28}$$

The quantity r_1 is independent of λ and may be positive or negative.

Because the refractive index μ_0 and the extinction coefficient κ_0 occur explicitly in (28) and the constants of the Lorentz dispersion equation (23) do not occur therein, we may proceed as is often done in theoretical physics. We may discard the scaffolding by means of which the equation (28) has been built up and, without troubling ourselves any more about the theory of electrons we may postulate equation (28) as a concise description of the phenomenon in any medium, no matter whether the refractive index and extinction coefficient of the medium do or do not satisfy the Lorentz dispersion equation. It remains to substantiate this by experiment.

UNIVERSITY OF IOWA,
IOWA CITY,
November, 1922

INTRINSIC MAGNETIC FIELDS

By Leigh Page

Abstract

Emission theory of electromagnetic fields.—(1) *Intrinsic magnetic field.* The intrinsic magnetic field of a point charge is defined as that portion of the field which cannot be annihilated by the Lorentz transformation. It is shown that the intrinsic field can be represented by lines of force carried by the same moving elements as carry the electric field, and a potential is given for it. (2) *Frequency of emission of moving elements.* A relation between the frequency of emission of moving elements and the number of lines of force to a tube is deduced on the assumption that the latter number is the same for the electric and magnetic fields and that each moving element marks the intersection of an electric and magnetic line of force.

IN PREVIOUS papers[1] the author has presented a simple and rigorously accurate kinematical representation of the laws of electromagnetism. In this representation each element of charge is supposed to be the source of discontinuities, or moving elements, shot out from it uniformly and continuously in all directions with the velocity of light. A *line of electric force* is the locus of those moving elements emitted in a given direction. If the charge is accelerated so as to pass in a time dt from a system S to a system S', a moving element emitted by the charge while in S' is considered to be emitted in the same direction as another moving element emitted while the charge is in S if the velocities of the two moving elements lie in the same plane and make equal angles with the direction of the acceleration, each angle being measured in the system in which the charge is at rest at the instant of emission. The four field equations of electromagnetism follow as necessary consequences of this representation, and the only additional assumption required in order to deduce the force equation is Lorentz's postulate that the resultant force on an electron or proton vanishes.

In the kinematical relations deduced on the basis of the above representation the vector

$$\mathbf{H} \equiv \frac{1}{c} (\mathbf{c} \times \mathbf{E}), \tag{1}$$

where $\mathbf{c}$ represents the velocity of the moving elements at the point in question and $\mathbf{E}$ is the electric intensity, takes the place of the magnetic

[1] Page, Relativity and the Ether, Am. Jour. Sci. **38**, 169, 1914; An Introduction to Electrodynamics, Ginn and Co., 1922. Page references in the text are to this book.

intensity in the usual formulation, and is therefore identical with this quantity. As the divergence of the magnetic intensity is everywhere zero, it can be represented by continuous lines of force throughout the field. The question then arises: How far may the *same* moving elements which carry the lines of electric force also serve as carriers of the lines of magnetic force? When connected in the manner already described, the loci of the moving elements emitted by an element of charge constitute lines of electric force; can the same moving elements be strung together in a different way so that the new loci shall constitute lines of magnetic force?

This question has been answered in part in the book[1] already referred to (page 63). It is shown there that the moving elements which carry the electric lines of force cannot in general carry the magnetic lines, although under such conditions as exist in a wave front, the same moving elements serve both fields. The object of this paper is to present a more complete answer to the question proposed.

In the first place, it is clear that a field which can be transformed away by a change in the observer's state of motion cannot be represented by moving lines of force of the kind employed in the original representation. For a change in the observer's state of motion merely changes his point of view, altering, perhaps, the density and direction of the lines of force but annulling none of them. Hence the magnetic field of a charge moving relative to the observer with constant velocity, since it can be annihilated by the Lorentz transformation, is not susceptible of representation in the manner adopted for the electric field. Therefore it is convenient to consider the magnetic field due to an element of charge to be composed of two parts; *the intrinsic field*, which cannot be transformed away, and *the apparent field*, which is dependent on the state of motion of the observer and can be annihilated by the Lorentz transformation.

To determine the intensity of the intrinsic field, consider an element of charge which is momentarily at rest relative to the observer but has an acceleration f (Fig. 1). The retarded magnetic field at P is (page 27)

$$\mathbf{H}_p = \left[\frac{e}{4\pi r_p c^3}\mathbf{f}\times\mathbf{c}\right]. \tag{2}$$

This retarded expression gives the field at P at a time OP/c later than the time 0 at which e was at rest at O and had the acceleration f. The lines of force are circles with centers on the line drawn through e in the direction of $\mathbf{f}$. Now the field at Q at the time OQ/c is given by the same expression provided $r_p \equiv OP$ is replaced by $\mathrm{r}_Q \equiv OQ$, that is

$$\mathbf{H}_q = \left[\frac{e}{4\pi r_q c^3}\mathbf{f}\times\mathbf{c}\right]. \tag{3}$$

But it is evident from the figure that if the lines of force present at P at the time OP/c move out with the velocity of light along radii vectors drawn from O, the number of tubes of force per unit cross-section at Q at the time OQ/c is just that requisite to give equation (3). Now this motion is exactly that of the moving elements which carry the electric lines of force. Therefore the field (2) is carried by the same moving elements as constitute the electric lines of force. Hence it constitutes at least a *part* of the intrinsic field, and as it is the only magnetic field relative to the observer considered, it must constitute the *entire* intrinsic field.

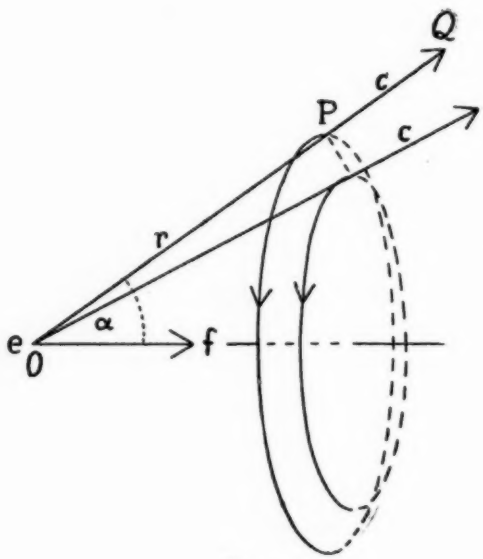

Fig. 1

In order to find the intrinsic field of a charge which is moving with velocity v relative to the observer, consider a system S' moving along with the charge. In S' the intrinsic field $\mathbf{H}'_i$ is

$$\mathbf{H}'_i = \left[\frac{e}{4\pi r' c^3}\ \mathbf{f}' \times \mathbf{c}'\right]$$

Transformations for any vector field all points of which are moving with the velocity of light have been given (page 23). If v is in the X direction these are

$$\mathrm{H}_x = \mathrm{H}_x'$$

$$\mathrm{H}_y = k\left\{\mathrm{H}_y' + \frac{\beta}{c}(\mathbf{c}' \times \mathbf{H}')_z\right\},$$

$$\mathrm{H}_z = k\left\{\mathrm{H}_z' - \frac{\beta}{c}(\mathbf{c}' \times \mathbf{H}')_y\right\}.$$

Making use of these, it is easily shown that

$$\mathbf{H}_i = \left[\frac{e}{4\pi r c^5 (1-\mathbf{c}\cdot\mathbf{v}/\mathbf{c}^2)^3}\,\mathbf{c}\times(\{\mathbf{f}\times(\mathbf{c}-\mathbf{v})\}\times\mathbf{c})\right]. \tag{4}$$

The remaining portion of the field, that is

$$\mathbf{H}_v = \left[\frac{e}{4\pi r^2 k^2 c^2 (1-\mathbf{c}\cdot\mathbf{v}/\mathbf{c}^2)^3}\,(\mathbf{v}\times\mathbf{c})\right] \tag{5}$$

can be annihilated by the Lorentz transformation, and constitutes the apparent field due to the observer's state of motion.

As $\mathbf{H}_i$ is represented by continuous lines of force, the divergence of (4) should vanish. This may easily be verified by direct differentiation. In fact $\mathbf{H}_i$ is the curl of the retarded vector potential.

$$\mathbf{a}_i = \frac{e}{4\pi}\left[\frac{\mathbf{c}\cdot\mathbf{f}\,\mathbf{c}}{c^4(1-\mathbf{c}\cdot\mathbf{v}/\mathbf{c}^2)^2}\right],$$

and $\mathbf{H}_v$ the curl of

$$\mathbf{a}_v = \frac{e}{4\pi}\left[\frac{\mathbf{c}}{rk^2c(1-\mathbf{c}\cdot\mathbf{v}/\mathbf{c}^2)^2}\right].$$

The sum of $\mathbf{a}_i$ and $\mathbf{a}_v$ differs from the usual vector potential

$$\mathbf{a} = \frac{e}{4\pi}\left[\frac{\mathbf{v}}{rc(1-\mathbf{c}\cdot\mathbf{v}/\mathbf{c}^2)}\right]$$

by

$$\frac{e}{4\pi}\,\nabla\log\left[r(1-\mathbf{c}\cdot\mathbf{v}/\mathbf{c}^2)\right]$$

which, as its curl vanishes, contributes nothing to the value of $\mathbf{H}$.

It has been shown that the intrinsic magnetic field of an element of charge is carried by the same moving elements as serve to carry the electric field. Let it be assumed now that *every* moving element lies on both an electric line of force and a line of force of the intrinsic magnetic field, that is, at the intersection of two such lines. Furthermore, let it be assumed that the number M of lines of force constituting a tube is the same for the magnetic as for the electric field. Then a relation may be derived between the number ν of moving elements emitted by the charge along a line of electric force in a unit time (heretofore assumed immeasurably large) and the constant M. For the number of lines of electric force passing through a unit cross-section perpendicular to OP at P (Fig. 1) is $e\,M/4\pi r^2$, and the number per unit width of this unit square is

$$\frac{1}{r}\sqrt{\frac{eM}{4\pi}}$$

Along the radius vector the number of moving elements per unit length for each line of electric force is ν/c, so the number of lines of magnetic force per unit cross section is

$$M\,H \equiv \frac{eMf \sin \alpha}{4\pi r c^2} = \frac{\nu}{rc}\sqrt{\frac{eM}{4\pi}}$$

whence

$$\nu = \frac{f \sin \alpha}{c}\sqrt{\frac{eM}{4\pi}}$$

and the total number of moving elements emitted per unit time is

$$\frac{eM}{4\pi r^2}\int_0^\pi \nu 2\pi r^2 \sin \alpha d\alpha = \frac{f\sqrt{\pi}}{8\,c}\,(eM)^{3/2}.$$

As ν and M approach infinity together, the field may be made as nearly continuous as need be, both along and at right angles to the lines of force, by making M great enough.

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February 26, 1923.

THE TORQUES AND FORCES BETWEEN SHORT CYLINDRICAL COILS CARRYING ALTERNATING CURRENTS OF RADIO FREQUENCY

By W. A. Parlin

Abstract

Forces between two short cylindrical coils carrying alternating currents of frequency 60 to 1.5 x 10^6 cycles.—(1) Coils with a common diameter, mounted like a dynamometer, the outer coil being suspended and free to turn about the fixed inner one, were connected in series with the current in the same sense for zero angle. The torque was found proportional to the square of the current for all frequencies, but for a constant angle began to increase with the frequency at 3×10^5 cycles. The ratio of the torque for 15×10^5 cycles to that at 3×10^5 cycles decreased from two at 10° to one for 90° and remained one for all angles for which the currents were in opposite sense. In the case of 60 cycles, the variation of the torque with angle corresponded roughly with that computed from Maxwell's equations. (2) *Coils with planes parallel* showed a similar increase of force with frequency for frequencies above 3×10^5 cycles, when the currents were in the same sense, but not when they were in opposite sense. It is suggested that these variations with frequency may be due to the reactions caused by the radiation of energy from the coils in the form of electromagnetic waves.

Introduction

THE FORCES between circular currents have been the subject of considerable investigation both experimental and theoretical. Maxwell[1] has derived formulas which give the torques and forces between coils in various positions carrying electric currents. His formulas are valid for direct and slowly varying alternating currents. As far as is known no experimental work has been done to determine the torques and forces between coils carrying radio frequency currents, that is, frequencies of 10^4 to 10^7 alternations per second.

In the present work measurements have been made of the forces between circular coils in various positions, which carried direct current, 60 cycle alternating current, and currents of radio frequency. For the low frequency currents the torques and forces were found to conform to the usual formulas given by Maxwell and others, but in certain cases where radio-frequency currents traversed the coils, the measurements are not in agreement with the theoretical formulas.

[1] Maxwell, Electricity and Magnetism, Vol. II, 1873

Apparatus

To measure the torque between the two coils, a sensitive dynamometer arrangement was used which consisted of a fixed coil of 11 turns, 10 inches in diameter, and a movable coil of 11 turns, 12 inches in diameter, suspended outside of and free to turn about the fixed coil. Contact with the movable coil was made by mercury contacts. The suspension was a bronze wire 8.38 inches long and 0.005 inch in diameter. The upper end of the bronze wire was fastened to a dial which could be turned about the axis of suspension. To measure the torque, the dial was set so that the coils made a certain angle with no current flowing. With current through the coils a torque was produced which changed the angle between the coils. The dial was then turned so that the coils returned to the original angle. The difference in the readings denoted the torque between the coils. The two coils were in series with a carefully calibrated hot wire ammeter. For the radio-frequency currents a small coil was introduced in series with the dynamometer coils for coupling purposes. An electron tube oscillating circuit was the

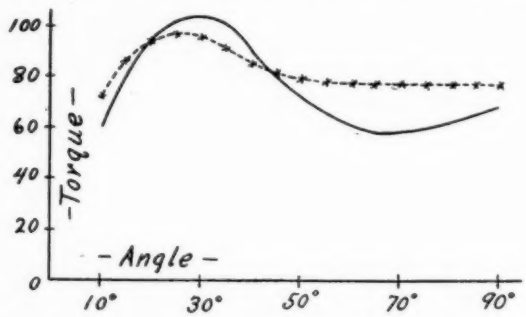

Fig. 1. Torque as function of angle, for 60-cycle current.

source of the undamped radio-frequency currents, and a one-half kilowatt transformer with a condenser and quenched spark gap, provided the damped radio-frequency currents.

Tests with slowly varying currents. Tests were made to see to what extent agreement between a theoretical formula and measurement might be expected. It was found that for a given angle between the coils the torque increased very closely as the square of the current, in accord with theory. For a constant 60 cycle current of 0.60 amperes the torque was measured for a series of angles between the coils, from 10° to 90°. The measurements are shown by the crosses and dotted curve of Fig. 1. The theoretical curve for this case, plotted from six terms of Maxwell's formulas (page 303, loc. cit.[1]), is given by the full line curve of Fig. 1. The agreement between the two curves is perhaps as close as could be ex-

pected because the formula refers to coils of a single turn whereas the coils in the present experiment were of finite length and had several turns of wire.

In all the figures the torques have been expressed in arbitrary units, actually in degrees. These values may be changed to dyne-centimeters by multiplying by 20.7.

The torque between coils carrying radio-frequency currents. In agreement with simple theory the torque between the coils for a constant angle

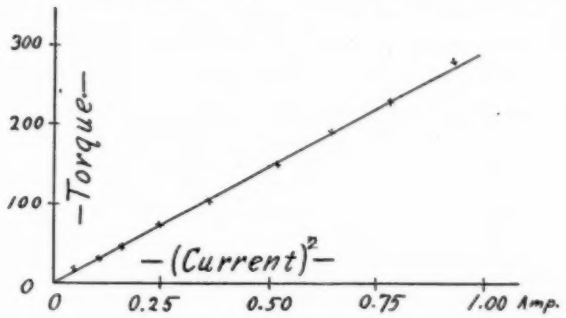

Fig. 2. Torque as a function of (current)², for frequency of 4×10^5 cycles.

of 30° traversed by a current of frequency 0.4×10^6 cycles (750 meters) varied directly as the square of the current. Fig. 2 gives the results of these measurements.

With the current through the coils in the same sense and the angle between the coils maintained constant, it was found that *the torque in-*

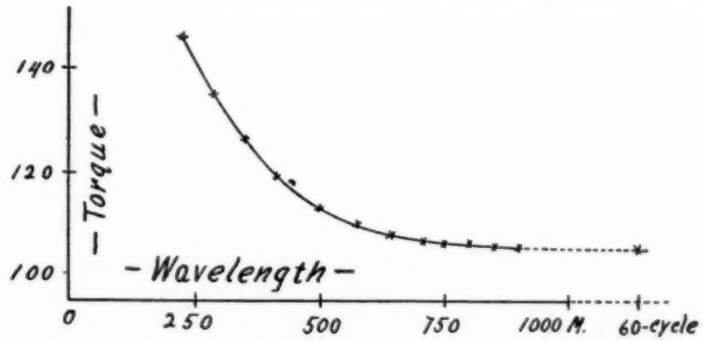

Fig. 3. Variation of torque with wave-length, for 22.5° angle.

creased with the frequency of the current. This is shown by Fig. 3 which was taken for a current of 0.60 amperes and an angle between the coils of 22.5°. The curve indicates that for the region between 60 cycles and about 700 meters no changes in torque with frequency of the current occurred, but that for the wave-lengths below 700 meters the torque

increased in a marked manner with the frequency. This increase in the torque with the frequency was not to be expected from the classical formulas of Maxwell, which contain no frequency term.

When the currents through the two coils were in the same sense, the change in torque with frequency was found to increase as the angle between the coils decreased. For angles between the coils from 90° to 270°, i.e., the currents being in the opposite sense, the torque did not change with the frequency of the current. These results are shown in Fig. 4 in which the percentage change in torque between wave-lengths 235 and 908 meters are plotted as ordinates against angles between the coils as abscissas. Similar results were obtained for damped radio frequency currents as for undamped currents.

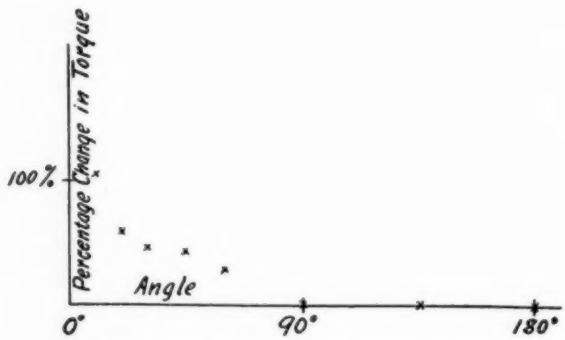

Fig. 4. Percentage excess torque for 235 meters as functions of angle.

The forces between parallel coils carrying radio frequency currents. The movable coil was arranged at the end of the bar of a torsion pendulum and the force between the two coils observed by means of a torsion head on the supporting wire of the pendulum. In the figures the forces are given in arbitrary degrees; these numbers may be reduced to dynes by multiplying by 1.16. For a constant distance between the two coils and with current of constant frequency, the force was found to increase directly as the square of the current, in agreement with simple theory.

With currents in the same direction in the two coils the force was found to increase with the frequency, the rate of increase of force with frequency depending upon the distance between the coils. Fig. 5 shows the force vs. wave-length curves for distance between the coils of 2, 4, 6, and 8 inches respectively, the current being 0.60 amperes in all cases. These results, as in the case of the torques, are at variance with the formulas for slowly varying currents. The percentage change in force

from wave-lengths 235 to 908 meters appeared to increase with the distance between the coils, as given in Fig. 6. Conclusions similar to those for the undamped currents were found to be true for damped radio frequency currents.

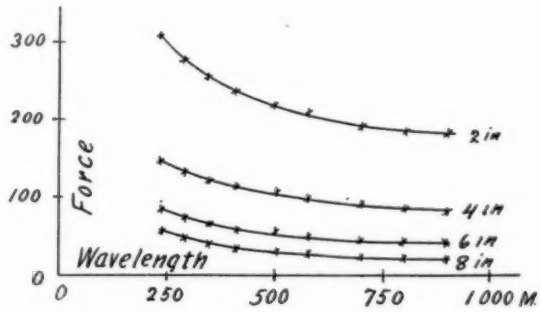

Fig. 5. Force between parallel coils as function of wave-length.

Discussion. From a consideration of the various phenomena of radio-frequency currents not taken into account by the classical theory it would seem that an explanation of the foregoing discrepancies between existing formulas and the present measurements is to be sought in the

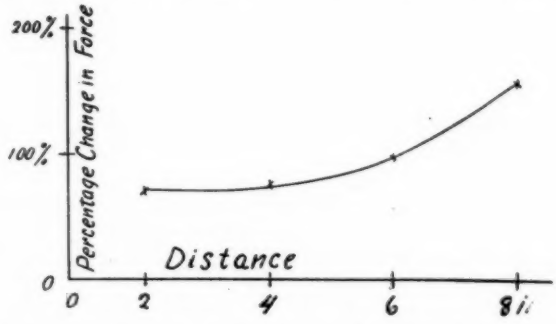

Fig. 6. Percentage excess force for 235 meters as function of distance apart of coils.

reactions caused by the radiation of energy from the coils in the form of electromagnetic waves.

In conclusion I wish to thank Dr. E. O. Hulburt for suggesting the problem and for his advice during the course of the work.

PHYSICAL LABORATORY,
STATE UNIVERSITY OF IOWA.
February 6, 1923

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE PASADENA MEETING, MAY 5, 1923

The 121st meeting of the American Physical Society was held in the Norman Bridge Laboratory of Physics, California Institute of Technology, Pasadena, California, on Saturday, May 5, 1923. The secretary of the Pacific Coast Section of the Society presided. The program was completed in two sessions with an attendance of about 150.

Abstracts of the thirty-three papers which were presented are given below, not in the order of presentation, but arranged according to subject. An **Authors Index** will be found at the end.

D. L. WEBSTER,
Secretary of the Pacific Coast Section.

ABSTRACTS OF PAPERS

1. Penetrating radiation at high altitudes. R. A. MILLIKAN and I. S. BOWEN, California Institute of Technology.—Kolhorster and others have observed an increase in the residual ionization in closed vessels at high altitudes. The variation of this ionization with altitude indicated a radiation of high penetrating power coming from outside the atmosphere. Our experiments which were made with recording electrometers carried by pilot balloons to altitudes of over 15 km indicate an increase of but 25 percent of that predicted from an extrapolation of Kolhorster's curve.

2. The variation of penetrating radiation with altitude. RUSSELL M. OTIS, California Institute of Technology.—There exists in the atmosphere a very penetrating radiation of the beta-gamma type, the intensity of which has been observed by Kolhorster, Hess and others to increase with altitude. The object of these experiments was to measure this increase, and, if possible, to determine the extent to which some suggested causes of its existence are operative. The instrument employed was a specially designed Wulf electroscope, very similar to the one used by Kolhorster, except that the insulation losses were counteracted by an electrical method. Measurements in airplanes and balloons to an altitude of 5340 m. indicate first a decrease, then an increase in radiation, the increase, however, being not so great as that found by Kolhorster. Kunsman (Phys. Rev., 16, p. 349, 1920) suggested, as a consequence of his experiments, that the increase was due to mistaking loss of charge by insulation leak for loss of charge by ionization, and that the greater insulation leak at high altitudes resulted from the lower temperature. Tests made on the electroscope used in these experiments, however, show no such effect to exist in that instrument. Some other cause must, therefore, be found to explain this increase in radiation with altitude.

3. The penetrating radiation on Mt. Whitney. RUSSELL M. OTIS. California Institute of Technology.—Measurements of the penetrating radiation were made at U.S.G.S. B.M. No. 15, Elevation 13552 ft, near the top of Mt. Whitney, California. Observations were made over consecutive two-hour periods for forty hours. No sensible difference could be detected between night and day values of the penetrating radiation. This indicates that the sun has no part in producing directly the radiation which we measure. The mean value of the ionization at this level was 19.6 ions/cc/sec as compared to 9.33 ions/cc/sec at Pasadena (elevation 800 ft). The mean of two observations at U.S.G.S. B.M. No. 14, elevation 12000 ft, was 17.3 ions/cc/sec. At this level the electroscope was floated on a lake, one meter deep, and the mean of two observations was 13.6 ions/cc/sec. The difference between land and water values at Pasadena is 3.0 ions/cc/sec. Inasmuch as this represents the radiation coming from the ground, it it concluded that the increase in ionization on Mt. Whitney over that in Pasadena is not due to greater radioactivity of the ground, but is the result of either a greater radioactivity of the atmosphere at that height or of a radiation coming into the atmosphere from some source other than the sun.

4. Critical potentials of thorium M series lines. P. A. ROSS, Stanford University.—A vacuum x-ray spectograph is described, in which a screen, rotated at twice the angle of the crys al, serves to prevent the x-rays scattered by the crystal, from striking the plate. Spectrograms show six M series lines corresponding to α, β, γ, δ and ϵ of Stenström and a new line ϵ_2 of wave-length 2.85 A. Five absorption limits were found. Two of them, 2.571 A and 2.388 A have recently been found by Coster. The critical potentials of the lines have been found to be:

	Line	Critical voltage	Absorption limit to which it is related
(α)	4.1292A	3.32 kv	(M_1)3.721A
(β)	3.9333	3.48	(M_2)3.552
(γ)	3.6565	4.05	(M_3)3.058
(δ)	3.127	4.80	(M_4)2.571
(ϵ_1)	3.006	4.80	(M_4)2.571
(ϵ_2)	2.85	5.10	(M_5)2.85

5. Some anomalous spots on Laue photographs. ROSCOE G. DICKINSON, National Research Fellow in Chemistry, California Institute of Technology.—A symmetrical cube-face Laue photograph of SnI_4 (J. Am. Chem. Soc., **45**, 958, 1923) showed eight diffuse spots symmetrically surrounding the central image. A slightly unsymmetrical photograph showed these spots unchanged in position (unlike the usual Laue spots) but altered in intensity; no definite indices could be assigned to them by the usual methods. Similar results were obtained with potassium iodide. As the specimens used were sections prepared by grinding with fine emery, the following hypothesis was made: There exist in the crystal a great number of small crystals individually perfect but with their axes slightly inclined to those of the main crystal, the number of individuals having a given inclination being smaller the greater the inclination. This assumption can account for the radial streaks frequently observed passing through intense Laue spots or through the central image; it makes the anomalous spots portions of such streaks reflected by faces of the forms $\{100\}$ and $\{110\}$ and limited by the critical absorptions of iodine and silver. The anomalous spots are thus a type of powder photograph produced by a narrow band of x-rays. The assumption has been tested in a number of ways.

6. Absorption curves for alum, Iceland spar, quartz, and thin glass. SETH B. NICHOLSON and EDISON PETTIT, Mount Wilson Observatory.—A plane parallel plate of potassium alum 1.67 mm thick absorbs radiation as a water cell does. For such

a plate the absorption begins at 1.0μ and increases rapidly until complete at 1.9μ. The alum plate makes an excellent screen for absorbing infra-red radiation. A plate of Iceland spar of the same thickness transmits radiation to 2μ, where the absorption begins. Between 3.3μ and 5.6μ the transmission is low and at 5.8μ complete absorption is reached. A microscope cover glass 0.165 mm thick transmits wave-lengths about 1μ longer than a plate of quartz 1.67 mm thick. For studying radiation such as that from the stars the thin cover glass makes an ideal window for radiation instruments. We have found, however, that a high vacuum can be maintained as easily with a thin rock salt window as with a glass window. The exposed surface stays transparent for a considerable time and when the surface has deteriorated it can be polished easily. On account of its transparency to all wave-lengths shorter than 16μ rock salt makes the most suitable windows for vacuum thermocouples.

7. **Harmonic relations in the infra-red absorption spectra of liquids.** JOSEPH W. ELLIS, University of California.—An automatic mechanism for recording absorption spectra in the near infra-red has been constructed. It consisted of a strip of sensitized photographic paper wrapped around a rotating drum, upon which a spot of light from the galvanometer played. A single shaft rotated both the drum and the flint glass prism. Some forty organic liquids, including certain hydrocarbons, aliphatic halides and organic oils, have been investigated. Using thicknesses varying from a thin film to 10 cm, absorption bands have been consistently found near $\lambda\lambda$ 2.3, 1.7, 1.38, 1.19, 1.03, 0.9, 0.83 and 0.76μ, whose presence has been ascribed to characteristic oscillation frequencies of the C-H bond. These appear to be respectively the second to the ninth harmonics of a fundamental band found near 6.9μ in Coblentz' curves (Publication of the Carnegie Institution No. 35, 1905) for organic compounds, the first harmonic also occurring near 3.4μ. Consistent values for the fundamental frequency ν_0 are obtained only when each frequency is expressed by $n\nu_0(1-nx)$, where $n=2$ for the first harmonic, etc., and x is a small correction factor. Two new bands were found in 10 cm cells of water at 0.845 and 0.745μ. These frequencies with those corresponding to known bands at 0.99, 1.185, 1.47, 1.98, 2.98 and 6μ, when plotted against harmonic numbers, assuming 6μ to be the fundamental, give a straight line relation.

8. **Features of the furnace and enhanced spectrum of titanium.** ARTHUR S. KING, Mount Wilson Observatory.—A study has been made of the furnace spectrum of titanium from λ 2700 to λ 3900, at various temperatures, to supplement data previously obtained for the visible spectrum. The lines are classified on the basis of the initial temperature at which they appear and the rate of change with temperature, according to the m thod used for other spectra. The characteristic of the furnace in bringing out many lines which are very faint in the arc was especially notable in this part of the titanium spectram, and resulted in the measurement of a large number of lines which have not been included in measurements of the arc spectrum. Another group of lines, very diffuse in the arc, were obtained sharp in the vacuum furnace, and yielded good measurements. The lines due to ionized titanium were readily selected by using a mixture with potassium chloride. The lower ionization potential of potassium caused a weakening of the enhanced lines of titanium. These lines constitute a large proportion of the titanium ultra-violet spectrum and are relatively easier to produce in the furnace than the enhanced lines of the visible region.

9. **A study of the green auroral line with the interferometer.** HAROLD D. BABCOCK, Mount Wilson Observatory.—The faint green spectral line, long recognized in the background of the night sky as identical with the most prominent line in the auroral spectrum, has been studied with the Fabry-Perot interferometer on Mount Wilson and in Pasadena. It can be photographed in one night with this instrument almost any time between the third and first quarters of the moon, even when the sky is partly

clouded. No prism or other dispersion apparatus is required. The etalon is mounted in front of a high speed camera using very rapid green sensitive plates and provided with a color screen when there is much moonlight or diffuse artificial light. Orders of interference amounting to 3700, 8450, 15500, 31000 and 85000 waves were successively used in photographing the interference rings, and from the sharpness it is concluded that the width of the line is not greater than 0.035 A. No evidence of complexity in the line structure has been noted. The surface brightness of the diffuse green auroral light has been found to be of the order of 10^{-3} times that of the green radiation from a mercury arc in vacuum. This was derived from a comparison of exposure times used on the two ring systems respectively. The observations covered the period February to November, 1922, during which time appreciable variations of the brightness were found, amounting to three or four fold. Eleven determinations of the wave-length were made with the interferometer. Two pairs of planes, three different separations, and three pairs of metallic films, both gold and silver, were used. The green mercury line and the strongest yellow neon line were used as standards. The wave-length was found to be 5577.350 I. A., with an uncertainty of about ± 0.005 A. This is 0.48 A less than the value obtained by Slipher with a prismatic spectograph.

10. New regularities in the spectra of the alkaline earths. F. A. SAUNDERS, Harvard University, and H. N. RUSSELL, Princeton University.—Many lines of Ca, Sr, and Ba are combinations between terms of the known series and other triple or single terms. More than twenty new terms of this sort have been found, accounting for all the stronger lines. Some terms (p') combine only with p and P terms; others (d') with d, D, s, and S; others with f and F. They do not combine with one another. Combination series of type $2\pi - m\sigma$, $2\pi - m\delta$, have been found in the spark spectra of Ca and Ba. A new pp' group in Ca (near λ 2560) indicates that the neutral atom can contain more than enough energy to ionize it. Probably (as Bohr suggests) both valence electrons are shifted to outer orbits. When both fall back, a single quantum is radiated. There are three d' triplets for each element, each wider than the preceding, with inner quantum numbers 2, 1.0; 3, 2.1; 4, 3.2. The separation of corresponding triplets increases with atomic weight; those between the triplets are nearly constant. Attributing the former to quantized changes in the position of the "Atomrumpf," the latter may be ascribed to independent quantized shifts in the orbit plane of the inner valence electron.

11. The Zeeman effect for iron, chromium and vanadium, and a determinat'on of e/m. HAROLD D. BABCOCK, Mount Wilson Observatory.—Between λ2300 and λ6700 the Zeeman effect has been measured for 1177 lines of Fe, 1123 of Cr, and 1462 of V at field strengths of about 30,000 gauss. Measured separations have been made specific through division by field strength and by square of wave-length. To each component is assigned a fraction representing its relation to the normal separation. Tables include calculated specific separations based upon these fractions. The large amount of data makes it possible to ascertain the existence of large denominators such as 21, 11, 17, 14, 13. Three series of observations were made for determination of e/m by mean of the fundamental equation for the Zeeman effect. Field strengths, ranging from 24,290 to 31,880 gauss, were measured with a test coil, a ballistic galvanometer, and a mutual inductance carrying a known current in its primary. The normal separation corresponding to each field strength was obtained by measuring the separations for a selected group of well known lines of Cr, Zn, Cd, Ti and Ba, main dependence being placed upon 40 lines of Cr. The value of e/m is found to be 1.761×10^7, with an uncertainty of probably not more than 2 units in the last place.

12. Experiments on Compton's change in wave-length on scattering. P. A. Ross, Stanford University.—In a recent bulletin of the National Research Council, A. H. Compton reported experiments showing an increase in wave-length of x-rays

on scattering, and in a later paper before the American Physical Society he developed a theory which makes the amount of shift independent of the original wave-length according to the formula $\Delta\lambda = (2h/mc)\sin\frac{1}{2}\theta$. For 90° scattering, $\Delta\lambda = .0242$ A. The author has looked for this shift in visible light with negative results. A Lummer-Gehrcke plate of resolving power 360,000 was used and the scattered beam compared with the direct beam using the green mercury line. The scattering substance was a block of paraffin and scattering was at 180° so that the shift should have been about .048 A while the plate should resolve to .015 A. Multiple reflections between silvered glass surfaces to the number of 16 reflections at 180° were also tried with negative results. Compton used an ionization chamber in measuring the shift. The author has photographed the shift of the Mo α lines using a fixed crystal, a fine slit and exposure of 100 hours with a water-cooled molybdenum tube run at 30m-amp. 42 kv peak. Paraffin was the scattering substance and at 90° the shift was found to be −025 A. There was also a fainter unshifted line. Both lines were broad and hazy while the comparison spectrum on the same film, made with no change in spectrometer, was sharp, with α_1 and α_2 well separated.

13. A test of the Bohr-Sommerfeld theory of spectral lines. E. H. KURTH, Princeton University.—On the basis of the Bohr-Sommerfeld scheme of the atom one would expect that if the electron giving rise to the arc spectrum were displaced from its normal position in the $1S$ orbit to the $2p$ orbit, the atom ought to be capable of scattering frequencies corresponding to the lines $2p-mx$ of its spectrum. Electrons emitted by an oxide coated cathode of approximately twenty square inches area, were accelerated under a potential of five volts in freshly liberated mercury vapor. The lines $1S-2p$ *alone* were produced by direct impact of these electrons. The resulting concentration of atoms with electrons in the $2p$ states, however, was greatly augmented by the transference of the original radiation from atom to atom before it was finely absorbed by the tube. A water cooled mercury arc was used as a source, the various lines being isolated by means of Wratten filters. The light, after passing through a six foot column of the excited vapor, was examined with an echelon spectroscope. Under favorable conditions the lines 5461 A and 4358 A, which are subordinate to the $1S—2p$ transitions, suffered a loss in intensity estimated as from 10 to 20 per cent. It was not found possible to scatter noticeably the lines 5769 A and 5791 A even though a slight amount of ionization was permitted, indicating that the condition of mercury vapor close to the liquid surface is not favorable for the 1849 A transition.

14. Simultaneous action of an electric and a magnetic field on a hydrogen-like atom. PAUL S. EPSTEIN, California Institute of Technology.—Let a hydrogen-like atom with the nuclear charge κe be subjected to the action of a homogeneous electric field of strength E and at the same time of a homogeneous magnetic field of strength H. The general principles of quantization given by the author in a previous paper lead to the following expression for the energy of the atom in a stationary state characterized by the three quantic numbers n_1, n_2, n_3.

$$W = -(2\pi^2 k^2 \mu e^4/h^2 n_3^2) + (h^2/4\pi^2)\ [(f^2 + 2fgn_3 \cos\alpha + g^2 n_3^2)^{\frac{1}{2}} n_1 -$$
$$-(f^2 - 2fgn_3 \cos\alpha + g^2 n_3^2)^{\frac{1}{2}} n_2 + (f\,\delta \sin\alpha) n_3]$$

The notations are: e and μ the charge and the mass of the electron, h Planck's constant, c the velocity of light, and α the angle between the directions of the magnetic and the electric field. Moreover we use the abbreviations $f = \pi ek/cmh$, $g = 3E/2k\mu e$, and denote by δ a constant coefficient which, under different conditions, may assume the values $+1$, 0 and -1.

15. Rotational specific heat of hydrogen. RICHARD C. TOLMAN, California Institute of Technology.—It is shown from a consideration of infra-red rotation-oscil-

lation spectra, that the lowest possible azumuthal quantum number for the non-oscillating rotating molecule of the "dumb-bell" model can have only the values zero, one, or one-half. The rotational specific heat of hydrogen has already been calculated by Reiche (Ann. der Physik, **58**, 657, 1919) for the first two possibilities; this paper presents the results obtained for the third. The new curve agrees with the experimental data probably as well as any curve of Reiche's, and gives a somewhat lower value for the moment of inertia of the hydrogen molecule, thus possibly agreeing better with the conclusions which can be drawn from the many lined spectrum of hydrogen. It is pointed out that the new assumption has the advantage of making the lowest possible azimuthal quantum number the same both for oscillating and non-oscillating molecules, and leads to a very simple theory of quantization in space which makes the *a priori* probabilities for successive energy levels stand in the ratio of 1, 2, 3 etc., without the necessity of resorting to arbitrary or artificial exclusions. It is not believed that the simple "dumb-bell" model can be more than a first approximation or that the results yet warrant the definite conclusion that half quantum numbers are to be preferred. It seemed desirable, however, to present the results, first as a natural extension of Reiche's work, and second, because half quantum numbers have recently shown a surprising tendency to appear.

16. Some consequences of the relativity theory of electronic orbits. G. E. GIBSON, University of California.—(1) The upper limit to the frequency of radiation emitted in any possible transition between orbits is m_0c^2/h. This follows from Sommerfeld's theory if we exclude orbits which collide with the nucleus as impossible. (2) The highest atomic number for which orbits of unit azimuthal quantum number are possible is 136. Orbits of azimuthal number n collide with the nucleus when n is not greater than αZ, where Z is atomic number and α is Sommerfeld's constant. Hence, $z=1/\alpha$ if $n=1$. Since Z is essentially integral, $1/\alpha$ should be integral. This is so within error limits. Taking $e=4.774\times10^{-10}$ and $e'/m_0=1.773\times10^{7}$, the equation $c\alpha^3=4\pi Re(e'/m_0)$ gives $1/\alpha=137.0\pm.1$. Hence, 136 is the highest atomic number for which K orbits exist. (3) The number 136 corresponds to the seventh rare gas of the periodic system. The number of elements in periods ending with rare gases are 2×1^2 (He), 2×2^2 (Ne), 2×2^2 (Ar), 2×3^2(Kr), 2×3^2(Xe), 2×4^2 (Em). Where there is no duplication the next number is the next term of the sequence $2\times n^2$. Chemical evidence shows that the period 2×4^2 is not duplicated, hence the number of elements in the seventh period should be $2\times5^2=50$. This gives 136 for the atomic number of the rare gas following emanation.

17. Possible isotopes of the elements. S. R. COOK, College of the Pacific.—1. General equations for two or more isotopes. Let α represent the helium atom; δ the hydrogen atom; 2δ the hydrogen molecule; a, b, c, d, etc., the isotopes of the particular element; x, y, z, w, etc., the fractional parts of the a, b, c, etc. isotopes; and w the atomic weight of the element. We may write for any element having two isotopes of the α, 2δ, or δ type, $x+y=1$ (Eq. 1), and $ax+by=w$, (Eq. 2). For any element of three or more isotopes, of the α, 2δ, or δ type or any combination of these, we have, $x+y+z+\text{etc.}=1$ and $ax+by+cz+\text{etc.}=w$. 2. Isotopes based on the α, 2δ, and δ types. (1) When isotopes are based on helium, $b-a=\alpha$, (2) when isotopes are based on hydrogen molecule, $b-a=2\delta$, and (3) when isotopes are based on the hydrogen atom, $b-a=\delta$. To illustrate; for the element copper ($w=63.57$), for (1), $b=64$, $a=60$; (2) $b=64$, $a=62$; (3) $b=64$, $a=63$. With these values of a and b equations (1) and (2) are solved. 3. The isotopes of all the elements according to the α, 2δ and δ types have been tabulated by solving equations (1) and (2). The values of x and y are given only for the elements with two isotopes. No general table for an element with three isotopes is possible.

18. The wave theory and the quantum theory. C. G. DARWIN, California Institute of Technology.—A review of work connected with the theory of dispersion described at the Christmas meeting of the American Physical Society. (Abstract, Phys. Rev. **21**, p. 377, 1923.)

19. Ferromagnetism and quantum theory. PAUL S. EPSTEIN, California Institute of Technology.—A critical review of the experimental data on the susceptibilities of ferromagnetic salts was recently published by B. Cabrera. This review seems to support the point of view taken in the theory of quanta. In fact, according to this theory the paramagnetic susceptibility is completely determined by the "inner quantic number" j, corresponding to the total moment of momentum of the atom or ion. The following table gives the calculated susceptibility (for unit mass) for different values of j and the measured susceptibilities for different ions:

j	Ion	$\chi \cdot 10^4$ calc.	$\chi \cdot 10^4$ obs.
0	Cu^+	0	0
1	Cu^{++}	1.0	1.1
2	Ni^{++} unsaturated	2.5	2.3
3	Ni^{++} saturated	4.8	3.5
	Cr^{+++}		5.0
4	Co^{++}	7.7	7.9
	Cr^{++}		7.9
5	Fe^{+++}	11.3	11.5
	Mn^{++}		11.6

It will be seen that the only discrepancy exceeding the limits of experimental error exists in the case of saturated Ni^{++} salts.

20. A correlation between the mechanical hardness and the magnetostrictive effects in ferromagnetic substances. Part 1. S. R. WILLIAMS, California Institute of Technology.—In studying the changes in length due to a magnetic field which occur in steel rods of a definite carbon content, it has been found that different annealing temperatures of a group of rods quenched at 788° C give different changes in length depending upon the duration of the annealing process. This type of magnetic analysis of mechanical properties reveals definite relations between the magnetic and mechanical characteristics of steel. It is being extended to all sorts and conditions of ferromagnetic substances in the hope that more light may be thrown on the physical meaning of what is termed "hardness of metals."

21. Hardness of steel balls by means of magnetic tests. S. R. WILLIAMS, California Institute of Technology.—It has been demonstrated that there is a definite relation between the magnetic properties of steel and its mechanical hardness. In general, the harder a steel, the less is its permeability. Using this relation, the magnetic field about a horse-shoe magnet is distorted by placing a steel ball between the poles of the magnet which, in turn, changes the deflection of a magnetometer controlled by the magnet. The softer the steel ball the more the field is distorted and the greater the deflection of the magnetometer. A study of the hardness of steel balls at different drawing temperatures shows that it is very easy to sort steel balls of a given size according to their degree of hardness. Balls supposed to have had the same heat treatment show differences. By this method the poor ones may be readily picked out.

22. A simple method of determining the components of the earth's magnetic field. S. R. WILLIAMS, California Institute of Technology.—In studying the Joule magnetostrictive effects in nickel, it was found that nickel was extremely sensitive to the effects of any extraneous magnetizing forces. If the nickel rod was demagnetized in the presence of a steady magnetic field, the rod was always found to be magnetized in

the direction of the extraneous field, (Amer. J. of Sci., **36**, p. 560, 1913) even for extremely small fields. This observation has led to the following method of determining the earth's field. A short nickel rod is surrounded by two small coils and set in the magnetic meridian. By one coil a steady magnetic field is maintained and through the other is passed a decreasing alternating current for demagnetizing purposes. Near one end of the nickel rod a magnetometer needle is suspended. The rod is demagnetized in various steady fields opposing that of the earth's field, until zero deflection is attained. At this point the opposing field is just equal to the earth's field. The method is very sensitive and accurate. A small form may be a tached to a surveyor's transit, using the compass needle as the magnetometer needle. This combination enables one to determine all of the components of the earth's magnetic field.

23. Variations in certain electrical systems inside a hollow conductor. JOSEPH G. BROWN, Stanford University.—The experiment described by Sanford at the Berkeley meeting in 1921 has been repeated in a slightly modified form. The electrometer, battery and insulated body were enclosed in a tight, zinc-covered wooden box with a glass window covered with wire netting. The electrometer is not affected by exterior electric charges, magnetic fields or changes in temperature. If one terminal of the battery is connected to the box, the electrometer goes through a daily cycle which approximates a sine graph, the maximum and minimum shifting from day to day. If the connection between battery and box is broken the electrometer drifts to a new position and then remains at rest. Since the electrical system inside the box is the same in both cases, it would seem that the variations are not due to changes in the system itself. A possible ionization current between the insulated body and the box is now being investigated. Sanford maintains that these variations are due to changes in the negative charge of the earth produced by induction from the sun and moon. Considering the fact that a result of this kind is quite contrary to generally accepted theory, it seems important to discover if possible the cause of the variation. Neither the daily curves nor the mean curves so far obtained correspond at all closely with Sanford's curves. This seems to indicate that the cause is more local than Sanford's theory would demand.

24. Is the ether a form of electricity? H. BATEMAN, California Institute of Technology.—Vectors E and H satisfying Maxwell's equations may be mean values of certain primary field vectors E' and H' which vary rapidly from point to point and are associated with a volume distribution of electricity. If in an electrostatic field the mean value of E' over the surface of a sphere of radius a is the value of E at the center we may write $E' = -grad\ V'$ where $V' = \Sigma(1/r)f(r)$, $f(r)$ being a periodic function of period $2a$. If the possible forms of electricity are determined by a balance of forces, then, in addition to the electron and proton there may be a form which moves with the velocity of light, but with finite energy, the electromagnetic force on each element of electricity vanishing in the absence of an external field as in the fields studied by J. J. Thomson and Levi Civita.

25. Vibration of strings excited by impact. S. H. ANDERSON, University of Washington.—Photographs have been made on moving films of the motion of a piano hammer in striking a string, and also of the vibration of a very short segment of the string, taken at various points along the string. Analysis by means of a harmonic analyzer of the curves so obtained shows that the measured amplitudes of the component sine curves do not agree with Hemholtz's theory of "struck" strings. Furthermore the time of contact between the hammer and the string is larger than he assumed and the string is given a displacement at the striking point during contact, which is contrary to his theory. Consequently an expression for the relative intensity of the partials of a struck string must be developed from a viewpoint different from that used by Hemholtz.

26. A method of measuring the velocity of sound in metallic vapors at very high temperatures. J. A. ANDERSON, Mount Wilson Observatory.—In this method the rise in temperature due to the adiabatic compression in a sound pulse is utilized. The metallic vapor at a very high temperature is produced by electrically exploding a fine wire. The sound pulse from the explosion, reflected by a cylindrical mirror falls on the hot vapor after a time interval which depends upon the distance between the wire and the mirror. The phenomenon is projected end-on upon the slit of a special rotating mirror camera, with the result that the passage of the sound wave through the vapor is photographed as a brighter line crossing at an angle the image of the explosion as lengthened out into a band by the rotating mirror. From the data thus obtained the velocity of sound in the vapor is easily calculated. For iron vapor the values found range between 1650 meters per second at 1/25,000 second after the beginning of the explosion and 990 meters per second at 1/3000 second.

27. On the progressive change of frequency in elastic waves. JAMES B. MACELWANE, University of California.—In the classical theory of elastic waves no provision is made for a change of period as the wave travels. The existence of such a phenomenon has been denied by Gutenberg and Roesener, and affirmed by Prince Galitzin, K. Wegener and Angenheister. Waves of so great energy are needed to furnish the required length of path that the present investigation was based on the waves sent out by the earthquake which occurred at 13h. 17m. 21s. $\pm$1s. G.M.C.T., January 31, 1922, off the coast of northern California, in Lat. 41° 8′$\pm$3′ N., Long. 125° 30′$\pm$3′W. The results were: (1) The period of a long, dilatational wave was found to decrease with the distance traveled, while that of a superposed short wave increased, the distinction disappearing at a surface distance of about 50° or 5565 km. (2) There seemed to be no functional relation between the periods of transverse waves in the interior of the earth and the length of path traversed. (3) The surface waves of the pseudo-Rayleigh group, while maintaining approximately constant velocity, were found to increase their periods at the average rate of 0.15 sec. per degree or 0.00136 sec. per km length of path, or 0.31 sec. per minute of travel time.

28. The quality of speech in auditoriums. V. O. KNUDSEN, University of California, Southern Branch.—Articulation tests, similar to those employed in telephone research, are being conducted to determine the quality of speech in the Millspaugh Auditorium at the Southern Branch of the University of California. There are four principal factors impairing the quality of speech in the auditorium, namely, extraneous noise, excessive reverberation, sound interference, and diminution of the intensity of the speech sounds toward the rear of the auditorium. The quantitative influence of each of these factors is determined by carrying out articulation tests for various conditions of noise, reverberation, and intensity. Observations are made by as many as 280 observers located in all parts of the auditorium. The articulation is as low as 30 per cent in the rear of the auditorium with no audience (reverberation = 5.3 seconds) and with the usual transit and conversation of students in the outside corridor. The elimination of this noise alone increases the articulation to 54 per cent. The articulation increases as the front of the auditorium is approached, and also increases as the size of the audience increases. Curves show the distribution of sound energy and the percentage articulation throughout the auditorium. Most errors occur with the consonant sounds, especially the final consonants. The consonant sound *ng* was mistaken 52 per cent of the total number of times it was called. The consonant sounds *th*, *d*, and *b* were mistaken nearly as frequently.

29. A definite art basis for the physical analysis of the quality o voice tones. L. E. DODD, University of California, Southern Branch.—In the analysis of voice tones outside of vowel quality in itself, judgment by musicians as to the quality of

the tones tested is necessary. Since the judgment given by an individual voice teacher or critic must be as representative as possible of the best musical taste, some formulation of what does and what does not satisfy critical musical taste is required. The author calls attention to a specific classification of tones as to their acceptable quality, based upon experiences that have become traditional among voice teachers, which furnishes a background and authority for such judgment.

30. New apparatus for determining the mass of the carrier in metals. RICHARD C. TOLMAN and LEWIS M. MOTT-SMITH, California Institute of Technology.—The apparatus used by Tolman, Karrer and Guernsey has been further modified by replacing the long torsion rods by much shorter helical springs, and by arranging for a continuous drive with a special bronze Pelton water wheel instead of using a reciprocating air piston. This will make it possible to orient the oscillating cylinder at different angles with respect to the earth's magnetic field and thus study more fully the possible accidental effect of the earth's magnetic field on the measurements. The continuous drive will also make it possible to generate alternating electromotive forces of variable phase which can be used in a null method for measuring the effect, in place of the deflection method previously used. This is important since it will make it possible to determine the phase relations in the electromotive force produced by the effect, and to eliminate the previous great uncertainty as to proper "zero correction" for the deflection. The apparatus was shown and briefly described.

31. A colorimeter for corrosive gases. E. C. WHITE and R. C. TOLMAN, California Institute of Technology.—An apparatus has been constructed for measuring low concentrations of corrosive gases such as bromine, iodine and nitrogen dioxide by matching the intensity of a long column with that of one of a series of shorter columns which form a connected system all containing gas of the same concentration. The gas columns are confined *entirely in glass tubes* whose ends are sealed with plane glass windows. The standard tubes are arranged on a cylindrical frame capable of rotating so as to bring them successively into the desired position for comparison with the sample tube and with a third very short tube which serves as the ultimate standard and is connected with a reservoir containing gas of high enough concentration to be susceptible of direct measurement. An optical system is provided for bringing the fields from the three tubes into juxtaposition and for assuring proper and uniform illumination. With the present apparatus much lower concentrations can be measured than by means of the glass pressure gages of Daniels and Bright, (J. Am. Chem. Soc. **42**, 1131, 1920) or of Karrer, Johnston, and Wulf, (J. Ind. and Eng. Chem. **14**, 1015, 1922).

32. The registering microphotometer of the Mount Wilson observatory. EDISON PETTIT and SETH B. NICHOLSON, Mount Wilson Observatory.—The purpose of this instrument is to register photographically the density gradient in a photographic negative. The photometer consists of a microscope with a screw driven stage on which the negative to be examined is placed. An image of a strongly illuminated slit placed below the stage is formed on the film of the negative. This illuminated strip of negative is again focused by the microscope objective upon a thermopile connected electrically to a Leeds and Northrup high sensitivity galvanometer. The stage-screw of the photometer is connected through a gear box and multiplier to the screw of a photographic registering device. This latter consists of a moving plate carriage, driven by a screw, which carries the plate past a cylindrical lens, 15 cm long with an 8 mm aperture made by sawing a glass rod in half, longitudinally. This lens functions as a slit with the advantage of large aperture. The plate carriage has a capacity for plates 15 cm by 1 m. The image of a strongly illuminated slit is made to play up and down the cylindrical lens as the galvanometer mirror swings. A motor driven cone wheel furnishes power to the screws. The whole instrument rests on a bed-plate 12 ft long by 28 inches wide.

33. A million volt transformer. ROYAL W. SORENSEN, California Institute of Technology.—The decision of the electrical engineers of the Southern Califo nia Edison Company and the California Institute of Technology to have equipment capable of producing low frequency alternating current potentials of 1,000,000 volts between a free and a grounded erminal made necessary the design of a special transformer. This transformer has just been completed. It consists of four separate transformers, each of which is placed on an insulating pedestal. The high potential from the first transformer is used to excite the second and that of the second to excite the third, and so on. In this way the voltage is built up to the desired value.

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BOOK NOTICES

Atoms. JEAN PERRIN. Translation by D. L. HAMMICK. (Second English edition, based on the 11th French edition, especially revised by the author and including his latest views on Radiation.)—The Chapter headings are: Chemistry and the Atomic Theory. Molecular Agitation. Brownian Movement; Emulsions. Fluctuations. Light and Quanta. Atom of Electricity. Genesis and Destruction of Atoms. Appendix 1921. XV+231 pp with index. Van Nostrand. 1923. $2.50.

Mirrors, Prisms and Lenses. JAMES P. C. SOUTHALL, Columbia University. (Enlarged and revised edition)—An introduction to the theory of modern optical instruments, intended primarily for elementary students and therefore employing only simple mathematics, but containing portions of value to the oculist and optometrist, including the fundamental principles of ophthalmic lenses and prisms. The first edition has been corrected, and besides many new problems, an appendix of 75 pp has been added. After seven chapters dealing with reflection and refraction of mirrors and lenses, are the following: Astigmatic Lenses. Geometrical Theory of the Symmetrical Optical Instrument. Compound Systems; Thick Lenses and Combinations of Lenses and Mirrors. Aperture and Field of Optical Systems. Optical System of the Eye; Magnifying Power of Optical Instruments. Dispersion and Achromatism. Rays of Finite Slope; Spherical Aberration. Astigmatism of Oblique Bundles, etc. Appendix: Miscellaneous Notes and Additions. VI+657 pp, 286 figures, and index. Macmillan. 1923.

Practical Optics for the Laboratory and Workshop. B. K. JOHNSON, Imperial College of Science, South Kensington.—Intended as an elementary laboratory course of instruction to prepare students for more advanced optical work; also to provide suggestions and information of practical value in the optician's workshop. Needed apparatus is described, often with scale drawings. Among the chapters are: Mirrors and Lenses (Optical Bench Experiments). Photometry. Spectrometer measurements. Determination of Radii of Curvature of Surfaces. Focal Lengths of Thick Lenses and Lens Systems. Miscellaneous Advanced Experiments (Testing Optical Instruments). Refractometers. Application of Polarized Light. Appendix: Cleaning, Silvering, Grinding and Polishing, Cementing, etc. 189 pp, 139 figures, no index. Van Nostrand. 1923.

Elements of Applied Physics. ALPHEUS W. SMITH, Ohio State University.—Intended to meet the needs of students primarily interested in the practical applications of physics to agriculture, engineering and everyday life. Many illustrations of these applications have been given including modern developments such as the Coolidge x-ray tube, the audion, wireless telegraphy and telephony. To help make definitions and statements of laws more concrete, they are frequently followed by simple numerical examples. Discussion of fundamental matters is, however, greatly condensed and some teachers may think the treatment too loose to stimulate clear thinking. XIV+483 pp with tables and index, 425 figures. McGraw-Hill. 1923.

Manual of Physical Measurements. ANTHONY ZELENY AND HENRY A. ERIKSON, University of Minnesota. (Fifth Edition)—An outline of 102 laboratory experiments for the courses in general physics at the University of Minnesota, together with 37 experiments in electrical measurements for a junior course. For each experiment, brief, clear descriptions of apparatus and method used are given, and directions for manipulation which are intended to leave, as far as practicable, the details of adjusting the apparatus and of carrying out the experiment to the student, working under the supervision of an instructor. XVII+ 288 pp, 141 figures, 38 tables, and index. McGraw-Hill. 1923.